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LOUIS P. HAMMETT, PH.D., *Consulting Editor*

THE THEORY OF RATE PROCESSES

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LOUIS P. HAMMETT, PH.D., *Consulting Editor*

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The Theory of RATE PROCESSES

*The Kinetics of Chemical Reactions, Viscosity,
Diffusion and Electrochemical Phenomena*

KEITH J. LAIDLER
and HENRY EYRING

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To

HUGH STOTT TAYLOR

TO WHOM THIS BOOK OWES MUCH

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PREFACE

One of the major unsolved problems of physical chemistry has been that of calculating the rates of chemical reactions from first principles, utilizing only such fundamental properties as the configurations, dimensions, interatomic forces, etc. of the reacting molecules. During the decade that has just ended the application of the methods of quantum mechanics and of statistical mechanics has resulted in the development of what has become known as the "theory of absolute reaction rates," and this has brought the aforementioned problem markedly nearer solution. It cannot be claimed that the solution is complete, but one of the objects of this book is to show how much progress has been made.

It may be pointed out, incidentally, that the theory of absolute reaction rates is not merely a theory of the kinetics of chemical reactions; it is one that can, in principle, be applied to any process involving a rearrangement of matter, that is to say, to any "rate process." In this book special reference is made to chemical reactions of various types—homogeneous and heterogeneous—and also to viscous flow, diffusion, dipole rotation, electrolytic migration and the discharge of ions from solution. These topics do not, by any means, exhaust the possibilities of the method: they serve, however, to illustrate its power, and the authors hope that others will be stimulated by what has been already done to attempt further applications of the theory of absolute reaction rates.

Most of the subject matter of the present book has been hitherto available only in the form of papers in various scientific journals; of necessity, these have been very concise and consequently they may have appeared difficult to those unfamiliar with the subjects concerned. The opportunity has therefore been taken, with the additional space available, to develop the theoretical bases and to give the practical applications in somewhat greater detail. It cannot be pretended, however, that the book can be read without effort: a complete understanding of

the subject matter undoubtedly requires close attention, but the writers venture to hope that those who make the necessary effort will be amply rewarded. The most difficult section, for readers who are not acquainted with the methods of quantum mechanics, is probably Chap. II; the book has, however, been written in such a manner that the omission of this chapter will not interfere seriously with the appreciation of the remainder. Similar considerations apply to the development of the various forms of statistics in the first part of Chap. IV.

The material presented here is the work of many minds, more even than is implied by the numerous references to the original papers; the authors desire, therefore, to place on record their appreciation of the invaluable contributions made by their colleagues and collaborators. They also wish to express their thanks to the American Institute of Physics and to the New York Academy of Sciences for their courtesy in allowing them to reproduce figures and other material from the *Journal of Chemical Physics* and from the monograph entitled "Kinetics in Solution," respectively.

SAMUEL GLASSTONE,
KEITH J. LAIDLER,
HENRY FYRING.

PRINCETON, N. J.,
May, 1941.

THEORY OF RATE PROCESSES

CHAPTER I

INTRODUCTION

The Arrhenius Equation.—The modern development of the theory of reaction rates may be said to have come from the proposal made by S. Arrhenius¹ to account for the influence of temperature on the rate of inversion of sucrose: he suggested that an equilibrium existed between inert and active molecules of the reactant and that the latter only were able to take part in the inversion process. By applying the reaction isochore to the equilibrium between inert and active species, it can be readily shown that the variation of the specific rate of the reaction with temperature should be expressed by an equation of the form

$$\ln k = \ln A - \frac{E}{RT}, \quad (1)$$

where E is the difference in heat content between the activated and inert molecules and A is a quantity that is independent of or varies relatively little with temperature. Subsequently, the Arrhenius equation (1) was written in the equivalent form

$$k = Ae^{-E/RT}, \quad (2)$$

and it is now generally accepted that a relationship of this kind represents the temperature dependence of the specific rates of most chemical reactions, and even of certain physical processes (see Chaps. IX and X); provided that the temperature range is not large, the quantities A and E can be taken as constant. For reasons that will appear later, the factor A has sometimes been called the "collision number," but a more satisfactory term, which will be used throughout this book, is the "frequency factor." The quantity E is termed the "heat of activation"

¹ S. Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

or "energy of activation" of the reaction;* it represents the energy that the molecule in the initial state of the process must acquire before it can take part in the reaction, whether it be physical or chemical. In its simplified form, therefore, the problem of making absolute calculations of reaction rates involves two independent aspects: these are the derivation of the energy of activation and of the frequency factor, respectively.

Calculation of Energy of Activation. According to the radiation theory of chemical reaction, which at one time attracted much attention, the excess energy of an active (or activated) molecule was derived from radiation absorbed by the reacting substance.² Since a molecule can absorb only radiations of definite frequency, corresponding to the position of the absorption bands in its spectrum, it is seen that the radiation theory would require the energy of activation per molecule to be $n h \nu$, or possibly to the sum of two or more $n h \nu$ terms, where h is the Planck constant, ν is the frequency of the absorbed radiation and n is an integer. In other words, the activation energy should be equal to a whole number of quanta of the absorbed radiation or radiations. There appeared at first to be some support for this expectation; but it became clear in the course of time that there is, in general, no correlation between the activation energy of a reaction and the absorption frequency of the reacting molecule, and so this avenue of approach to the problem of calculating the energy of activation had to be abandoned. Although various suggestions were made as to the nature of activation energy, *e.g.*, vibrational energy, or kinetic energy along the line of centers of two colliding molecules, no satisfactory alternative method was proposed for the derivation of the activation energy from fundamental properties of the

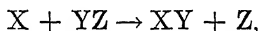
* Strictly speaking, the quantity E in Eqs. (1) and (2) is more correctly defined as the "experimental activation energy," for it is obtained in practice from the linear plot of the observed values of $\ln k$ against $1/T$, in accordance with the requirements of Eq. (1); the expression "heat of activation" should be reserved for a quantity, related to E , to which reference will be made later.

² See, for example, J. Perrin, *Ann. phys.*, [9] **11**, 1 (1919); W. C. McC. Lewis, *J. Chem. Soc.*, **113**, 471 (1918); *Trans. Faraday Soc.*, **17**, 573 (1922). See also G. N. Lewis and D. F. Smith, *J. Am. Chem. Soc.*, **47**, 1508 (1925); F. O. Rice, H. C. Urey and R. N. Washburne, *ibid.*, **50**, 2402 (1928); L. S. Kassel, *ibid.*, **51**, 54 (1929); F. Daniels, *Chem. Rev.*, **5**, 39 (1924).

reactants until 1928 when F. London³ indicated how the problem might be solved by the methods of quantum mechanics (see Chap. II). He suggested that many chemical reactions are "adiabatic," in the sense that they do not involve any electronic transitions; it is thus possible to represent the state of an electron by a single function applicable throughout the course of the chemical reaction. By making certain approximations, London derived an equation (see page 76) that may be used to give the variation with interatomic distances of the potential energy E of a system of three atoms, X, Y and Z, each having one uncoupled s -electron; this equation is

$$E = A + B + C - \{\frac{1}{2}[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2]\}^{\frac{1}{2}}, \quad (3)$$

where A , B and C are the coulombic interactions of the pair of electrons on the atoms X and Y, Y and Z and Z and X, respectively, and α , β and γ are the corresponding "resonance" or "exchange" energies, the latter being the quantum-mechanical consequence of the inability to regard an electron as located with respect to the nucleus with which it was associated in the separated atom. The values of A , B and C and of α , β and γ depend on the distance between the atoms, and by solving the appropriate integrals it should be possible to obtain a "potential-energy surface" giving the variation of potential energy for all possible interatomic distances. The reaction between the three atoms X, Y and Z, *e.g.*,



must then follow a path on this surface; most of the systems will naturally follow the easiest path. Even though the problem is simplified in practice by assuming a linear arrangement for three atoms and a planar one for four, as these can be shown to be the configurations requiring the minimum energy for a reaction involving s -electrons, the exact solution of the integrals which yield the separate coulombic and exchange energies is a matter of very great difficulty even in the simplest case, *viz.*,

³F. London, "Probleme der modernen Physik (Sommerfeld Festschrift)," p. 104, 1928; *Z. Elektrochem.*, **35**, 552 (1929). For other attempts to calculate activation energies, see R. M. Langer, *Phys. Rev.*, **34**, 92 (1929); D. S. Villars, *J. Am. Chem. Soc.*, **52**, 1733 (1930); J. Franck and E. Rabinowitsch, *Z. Elektrochem.*, **36**, 794 (1930).

two hydrogen atoms. The possibility of an approximate solution was considered by H. Eyring and M. Polanyi,⁴ who proposed what has become known as the "semi-empirical method" for the calculation of activation energies (Chap. III). The total binding energy of a pair of atoms,* *e.g.*, X and Y, is given by $A + \alpha$, and the variation with distance can be derived from spectroscopic data and expressed in the form of the familiar Morse equation (page 92). By making the assumption that A is a definite fraction of the total $A + \alpha$, generally 10 to 20 per cent, varying with the nature of the atom concerned, it is possible to obtain the individual values of A and α and similarly, also, of B and β and of C and γ , for various distances apart of the atoms. In this way, all the quantities are made available for the construction of the potential-energy surface by means of Eq. (3). The properties of such surfaces are considered in detail in Chap. III, but for the present it will be sufficient to indicate certain aspects only. It appears that as the reactant X is brought up to YZ, along the most favorable reaction path, the potential energy of the system increases at first slowly and then more rapidly to a maximum, and then decreases as the products $XY + Z$ are formed. The energy difference between the highest point in this path, which gives the position of the activated state, and the level representing the reactants is virtually equivalent to the activation energy of the reaction. It is thus possible to evaluate the latter from the potential energy for the system under consideration, and so the semi-empirical method gives a procedure for calculating, in certain cases, the energy of activation of a reaction from a knowledge of the spectra of the molecules obtained by considering the reacting atoms a pair at a time. The method has been subjected to some criticism, partly on account of the approximations involved in the derivation of the London equation and partly because of the assumption concerning the division of the total binding energy into definite coulombic and exchange fractions;

⁴ H. Eyring and M. Polanyi, *Z. physik. Chem.*, **B**, **12**, 279 (1931). See also H. Eyring, *J. Am. Chem. Soc.*, **53**, 2537 (1931); *Chem. Rev.*, **10**, 103 (1932); *Trans. Faraday Soc.*, **34**, 3 (1938).

* It is the practice to express the potential energy of a system of atoms with respect to the separated atoms as zero; in the combined state, therefore, the potential energy of the system is generally negative.

INTRODUCTION

but it will be seen in Chap. V that it has led to results which are in satisfactory agreement with experiment. Although it is admitted, therefore, that the treatment is incomplete, it is claimed, in default of any better method for the calculation of activation energies, that the semi-empirical procedure may be regarded as an important step forward in the development of the theory of reaction rates.

The Frequency Factor: Collision Theory.⁵—The exponential factor $e^{-E/RT}$ in Eq. (2) may be regarded as a measure either of the probability of the occurrence of the activated state or of the fraction of the total number of molecules that possess the requisite activation energy to enable them to take part in reaction; it is evident, therefore, that the factor A in Eq. (2) must have the dimensions of a frequency, so that the product $Ae^{-E/RT}$ may give the specific reaction rate. One view, which received support from many workers in the field of reaction kinetics during the second and third decades of the present century, was that for bimolecular gas reactions at least, A is equal to the frequency of collisions between reacting molecules in the gas; thus, in the case of reaction between two species A and B , the specific rate, assuming the standard state to be one molecule per cc., was represented by the expression

$$k = Z e^{-E/RT} \text{ cc. molecule}^{-1} \text{ sec.}^{-1} \quad (4)$$

where the collision frequency, or collision number, Z is given by the kinetic-theory equation

$$Z = \sigma_{A,B} \left(\frac{8\pi kT}{m_A m_B} \right)^{1/2} \left(\frac{m_A + m_B}{m_A m_B} \right)^{1/2}, \quad (5)$$

where $\sigma_{A,B}$ is the mean molecular (collision) diameter of A and B ; m_A and m_B are the actual masses of the respective molecules; k is the Boltzmann constant, *i.e.*, the gas constant per molecule. Since the expression for Z involves $T^{1/2}$, it follows from Eqs. (4) and (5) that

$$\ln k = (B + \frac{1}{2} \ln T) - \frac{E}{RT} \quad (6)$$

⁵ See W. C. McC Lewis, *J. Chem. Soc.*, **113**, 471 (1918); M. Polanyi, *Z. Elektrochem.*, **26**, 48, 228 (1920); K. F. Herzfeld, *ibid.*, **25**, 301 (1919); *Ann. Physik*, **59**, 635 (1919); C. N. Hinshelwood, "Kinetics of Chemical Change," Oxford University Press, 1940; *J. Chem. Soc.*, 635 (1937).

where B is a constant for the given reactants. It is seen that the frequency factor A , which is related to $B + \frac{1}{2} \ln T$ in Eq. (6), varies with temperature, and the plot of $\ln k$ against $1/T$ will not be exactly linear. If the temperature range is not great, however, the departure from linearity is small, and Eq. (4), which is the mathematical expression of the simple form of the "collision theory" of chemical reaction, may be regarded as equivalent to Eq. (2), the frequency factor being given by the collision number.

Since the collision number Z can be easily calculated, by use of molecular diameters derived from viscosity data or by being estimated in other ways, and B can be determined from the variation of the specific reaction rate with temperature, it should be possible to test the validity of the simple collision theory by seeing how far the results obtained from Eq. (4) are in harmony with experiment. This has been done for a variety of bimolecular reactions occurring in the gas phase and in solution, and in a number of instances the calculated rate constants agree, within a factor of 10, with the experimental values.⁶ Gas reactions involving simple molecules, *e.g.*, the combination of hydrogen and iodine and the decomposition of hydrogen iodide, are said to be "normal" reactions in the respect that their rates are in reasonable agreement with the requirements of Eq. (4). In general, the rates of reactions in the liquid phase that involve a simple ion, *e.g.*, the reaction between an ethyl halide and the hydroxyl ion or certain alkoxy ions, are in fair quantitative agreement with the collision hypothesis. There are, however, many instances of so-called "slow" reactions in solution, with rates much slower than would be expected from Eq. (4). Reactions of the Menschutkin type, *i.e.*, the addition of an alkyl iodide to a tertiary amine, are typical of many processes in solution that take place at rates which may be as small as 10^{-8} times the calculated values. It was thought, at one time, that the slowness of many reactions in solution was due to deactivation of the active molecules by collision with molecules of solvent; but several of the same processes were shown to occur just as slowly, or slower, in the gas phase.⁷

⁶ For summary, see E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," p. 74, Oxford University Press, 1933.

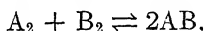
⁷ E. A. Moelwyn-Hughes and C. N. Hinshelwood, *J. Chem. Soc.*, 230

Numerous other gas reactions have also been found to take place very much more slowly than would be expected from the simple collision theory, and in order to overcome the difficulty raised by the existence of these "slow" reactions, Eq. (4) was modified by the introduction of a factor P ; thus

$$k = PZe^{-E/RT} \quad (7)$$

where P is referred to as the "probability" or "steric" factor. The value of P is a measure of the deviation of an actual reaction from the "ideal" behavior of the simple collision theory. Many attempts have been made, by the introduction of subsidiary hypotheses, to account for the small magnitude of P , varying from 10^{-1} to 10^{-8} , in the "slow" reactions, but they can hardly be regarded as adequate.⁸ It may also be mentioned that the difficulty is accentuated by the occurrence of reactions, particularly between ions in solution, in which P is greatly in excess of unity (see page 435).

An essential weakness of the collision hypothesis becomes evident when reversible reactions are considered:⁹ for the reaction



for example, the specific rate of the forward reaction should be given by

$$k_1 = Z_1e^{-E_1/RT}, \quad (8)$$

and that for the reverse reaction by

$$k_2 = Z_2e^{-E_2/RT}. \quad (9)$$

Consequently, k_1/k_2 , which is equal to the equilibrium constant of the system, may be written

$$K = \frac{k_1}{k_2} = e^{-(E_1-E_2)/RT}, \quad (10)$$

(1932); *Proc. Roy. Soc.*, **131**, A, 177 (1931); E. J. Bowen, E. A. Moelwyn-Hughes and C. N. Hinshelwood, *ibid.*, **134**, A, 211 (1931); G. H. Grant and C. N. Hinshelwood, *J. Chem. Soc.*, 258 (1933); H. W. Thompson and E. E. Blandon, *ibid.*, 1237 (1933); H. W. Thompson, C. F. Kearton and S. A. Lamb, *ibid.*, 1033 (1935).

⁸ Cf. C. N. Hinshelwood and C. A. Winkler, *ibid.*, 371 (1936); R. A. Fairclough and C. N. Hinshelwood, *ibid.*, 538 (1937); C. N. Hinshelwood, *ibid.*, 635 (1937).

⁹ A. E. Stearn and H. Eyring, *J. Chem. Phys.*, **3**, 113 (1937).

since Z_1/Z_2 cannot differ significantly from unity. The difference between the activation energies for forward and reverse reactions is equal to ΔH , the difference in heat content of the products and reactants, and so the simple collision theory leads to the requirement that

$$K = e^{-\Delta H/RT}, \quad (11)$$

which can only be true either at the absolute zero or if the reaction involves no entropy change. If the steric factors P_1 and P_2 are introduced for the two reactions, it follows that

$$K = \frac{k_1}{k_2} = \frac{P_1 Z_1}{P_2 Z_2} e^{-\Delta H/RT} \quad (12)$$

and hence $P_1 Z_1/P_2 Z_2$, or approximately P_1/P_2 , must in general involve an entropy term. Since the equilibrium constant K , which is equal to the ratio of the specific rates of forward and reverse reactions, is equal to $e^{-\Delta F^\circ/RT}$, where ΔF° is the standard free-energy change of the reaction, it would seem more reasonable to write, as was suggested many years ago,¹⁰

$$k = A e^{-\Delta F^\ddagger/RT} \quad (13)$$

$$= A e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}, \quad (14)$$

where ΔF^\ddagger , ΔH^\ddagger and ΔS^\ddagger are the free energy, heat and entropy of activation, respectively. A modification of the collision-theory equation, of the form of Eq. (14), viz.,

$$k = Z e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \quad (15)$$

has also been proposed to take into account the variation of the experimental activation energy with temperature.¹¹ According to the theory of reaction rates developed in this book, the factor determining the rate of reaction is not the heat of activation but the free energy of activation, and equations of the form of (13) and (14) should be employed. If the simple equation (2)

¹⁰ P. Kohnstamm and F. E. C. Scheffer, *Proc. Akad. Wetensch. Amst.*, **13**, 789 (1911); F. E. C. Scheffer and W. F. Brandsma, *Rec. trav. chim.*, **45**, 522 (1926); W. F. Brandsma, *ibid.*, **47**, 94 (1928); **48**, 1205 (1929).

¹¹ V. K. LaMer, *J. Chem. Phys.*, **1**, 289 (1933); see also V. K. LaMer and M. L. Miller, *J. Am. Chem. Soc.*, **57**, 2674 (1935); E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, **164**, A, 295 (1938).

is employed, it should be remembered that E , the experimental activation energy, varies with temperature to some extent, and A involves an entropy term.

Unimolecular Reactions.—Since the rate of a unimolecular reaction is proportional to the concentration of the reacting gas, *i.e.*, the number of molecules in a given volume, it seemed unlikely that the chemical change could be a direct consequence of collisions, since the collision frequency depends on the square of the number of molecules in unit volume of a single reactant. It appeared reasonable, therefore, to identify A with the vibration frequency (ν) of one of the bonds of the reacting molecule and to write

$$k = \nu e^{-E/RT}, \quad (16)$$

since $\nu e^{-E/RT}$ might be regarded as giving the rate at which sufficient energy was made available to permit the vibration to become so vigorous as to break the bond and hence lead to decomposition of the molecule. The view that the frequency factor A represents a vibration frequency was also regarded by some writers as applying to bimolecular reactions.¹²

The identification of A with a vibration frequency does not, however, overcome the difficulty of explaining how the molecule acquires its activation energy: the views expressed by F. A. Lindemann,¹³ however, received much support. It was suggested that a reacting molecule acquires its activation energy as the result of a collision, but there is a definite time lag before it decomposes. If, however, the average time interval between activation and decomposition is large in comparison with the interval between successive collisions, the process is kinetically of the first order, in spite of the fact that two molecules are involved in the collision (see page 282). It would appear, in these circumstances, that Eq. (4) should give the maximum reaction rate, whereas it is found in practice that the observed specific rates of many unimolecular gas reactions are several powers of 10 greater than that calculated from this equation.

¹² E. K. Rideal, *Phil. Mag.*, **40**, 461 (1920); S. Dushman, *J. Am. Chem. Soc.*, **43**, 397 (1921); K. F. Herzfeld, "Kinetische Theorie der Wärme," *Lehrbuch der Physik*, vol. III (2), Müller-Pouillet, p. 197, 1925. See also M. Polanyi and E. Wigner, *Z. physik. Chem.*, **139**, 439 (1928); H. Pelzer, *Z. Elektrochem.*, **39**, 608 (1933).

¹³ F. A. Lindemann, *Trans. Faraday Soc.*, **17**, 598 (1922).

It must be remembered, however, that the use of the term $e^{-E/RT}$ to represent the fraction of the colliding molecules that acquire the requisite activation energy is based on the assumption that the energy is available in *two* square terms only, *e.g.*, translational energy of each molecule along the line of centers, as has sometimes been supposed, or vibrational energy. If the energy from *several* square terms can contribute to the energy of activation, the proportion of molecules becoming activated on collision is greatly increased (page 283), and it appears that there is a rough parallelism between the complexity of the reacting molecule and the number of energy square terms which must be assumed in order to account for the observed reaction rates.¹⁴ Superficially, the general theory of unimolecular reactions, described above, with certain modifications that have been proposed (page 284),¹⁵ appears satisfactory; there is, however, the fundamental problem of why energy from several degrees of freedom should be able to contribute to the activation energy for a unimolecular reaction but not for a bimolecular process, even when relatively complex molecules are concerned.

Theory of Absolute Reaction Rates.—The method of calculating the frequency factor A , using the so-called "theory of absolute reaction rates," is elaborated in Chap. IV; it is based on the idea that a chemical reaction or other rate process is characterized by an initial configuration which passes over by continuous change of the coordinates into the final configuration. There is, however, always some intermediate configuration which is critical for the process, in the sense that if this system is attained there is a high probability that the reaction will continue to completion. This critical configuration is called the "activated complex" of the reaction,* and it is, in general, situated at the highest point of the most favorable reaction path on the potential-energy surface, to which reference was made on page 4. The activated complex is to be regarded as an ordinary molecule, possessing all the usual thermodynamic

¹⁴ C. N. Hinshelwood, *Proc. Roy. Soc.*, **113**, A, 230 (1926); R. H. Fowler and E. K. Rideal, *ibid.*, **113**, A, 570 (1927); see also Lewis and Smith, *Ref. 2*.

¹⁵ O. K. Rice and H. C. Ramsperger, *J. Am. Chem. Soc.*, **49**, 1617 (1927); **50**, 617 (1928); L. S. Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

* It is sometimes referred to as the "transition state." See, for example, M. Polanyi and M. G. Evans, *Trans. Faraday Soc.*, **31**, 875 (1935).

properties, with the exception that motion in one direction, *i.e.*, along the reaction coordinate, leads to decomposition at a definite rate. With these assumptions, it is possible to derive the concentration and rate at which the activated complexes pass through the critical configuration of the activated state by statistical methods, and the product of these quantities, as will be seen shortly, is equal to the reaction rate. It may be noted that somewhat similar ideas were put forward by A. Marce-
lin,¹⁶ who considered the rate of a process to be given by the rate at which the molecules crossed a "critical surface in phase space," and also by W. H. Rodebush,¹⁷ and particularly by O. K. Rice and H. Gershinowitz,¹⁸ who assumed that for a reaction to take place the system must lie in a "certain fraction of phase space." None of these authors, however, made use of the properties of the potential-energy surface which defines the precise nature of the activated complex, *i.e.*, the critical region of phase space, and so were unable to calculate absolute reaction rates. The first successful attempt in this direction was made by H. Pelzer and E. Wigner¹⁹ in their calculation of the rate of the reaction between hydrogen atoms and molecules, which is involved in the thermal homogeneous ortho-para conversion reaction. Various other authors²⁰ have also applied statistical methods to the theoretical treatment of reaction rates, but little progress could be made without a clear conception of the "activated complex" which H. Eyring showed to be the critical intermediate in every rate process. M. Polanyi and M. G. Evans, who also treated this problem, suggested the term "transition state" for this intermediate phase.²¹

¹⁶ A. Marceclin, *Ann. phys.*, **3**, 158 (1915); *cf.*, however, R. C. Tolman, *J. Am. Chem. Soc.*, **42**, 2506 (1920); **44**, 75 (1922); E. P. Adams, *ibid.*, **43**, 1251 (1921). See also A. March, *Physik. Z.*, **18**, 53 (1917).

¹⁷ W. H. Rodebush, *ibid.*, **45**, 606 (1923); *J. Chem. Phys.*, **1**, 440 (1933); **3**, 242 (1935); **4**, 744 (1936).

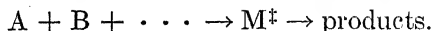
¹⁸ O. K. Rice and H. Gershinowitz, *ibid.*, **2**, 853 (1934); **3**, 479 (1935); G. B. Kistiakowsky and J. R. Lacher, *J. Am. Chem. Soc.*, **58**, 123 (1936).

¹⁹ H. Pelzer and E. Wigner, *Z. physik. Chem.*, **B**, **15**, 445 (1932).

²⁰ R. C. Tolman, "Statistical Mechanics," p. 259, Chemical Catalog Co., Inc., New York, 1927; La Mer, *Ref. 11*.

²¹ H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935); W. F. K. Wynne-Jones and H. Eyring, *ibid.*, **3**, 492 (1935); M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935); **33**, 448 (1937); M. Polanyi, *J. Chem. Soc.*, 629 (1937).

Consider a process involving the reactants A, B, etc., which form the activated complex M^\ddagger in the reaction



The rate of reaction is equal to the concentration of activated complexes at the top of the barrier multiplied by the frequency of crossing the barrier. If c_\ddagger' is the number of activated complexes in unit volume lying in a length δ representing the activated state at the top of the barrier, and \bar{v} is the mean velocity of crossing, then \bar{v}/δ is the frequency at which activated complexes pass over the barrier, and hence

$$\text{Rate of reaction} = c_\ddagger' \frac{\bar{v}}{\delta}. \quad (17)$$

The activated complexes differ from normal molecules in the respect that one of the degrees of vibrational freedom is replaced by translational motion along the reaction coordinate; these complexes can, however, be treated as normal molecules by writing their concentration at the top of the barrier as

$$c_\ddagger' = c_\ddagger \frac{(2\pi m^* kT)^{1/2} \delta}{h},$$

where m^* is the effective mass of the activated complex in the coordinate of reaction. The factor $(2\pi m^* kT)^{1/2} \delta/h$ is the partition function (page 168) for translation in the reaction path and represents the probability of the occurrence of the activated complex at the top of the barrier. By the use of classical methods the mean velocity (\bar{v}) of crossing the barrier in one direction, *i.e.*, in the direction of decomposition, is found to be $(kT/2\pi m^*)^{1/2}$, and hence Eq. (17) becomes

$$\text{Rate of reaction} = c_\ddagger \frac{(2\pi m^* kT)^{1/2} \delta}{h} \left(\frac{kT}{2\pi m^*} \right)^{1/2} \frac{1}{\delta} \quad (18)$$

$$= c_\ddagger \frac{kT}{h}. \quad (19)$$

The highly important consequence of the foregoing treatment is that the effective rate of crossing the energy barrier by the activated complexes is equal to kT/h , which is a universal frequency, dependent only on temperature and independent of the nature of the reactants and the type of reaction.²²

²² H. Eyring, Ref. 21. For review, see *idem*, *Chem. Rev.*, **17**, 65 (1935); *Trans. Faraday Soc.*, **34**, 41 (1938).

with a fair degree of accuracy. For stable molecules, particularly those whose spectra have been elucidated, the partition functions are known quite exactly; but even in other cases the values are not seriously in error. The equilibrium constant for any system can be expressed in terms of the partition functions of the molecules concerned, so that Eq. (22) may be written in the form

$$k = \frac{kT}{h} \frac{F_{\ddagger}}{F_A F_B} e^{-E_0/RT} \quad (25)$$

where F_{\ddagger} , F_A , F_B , etc., are the partition functions, per unit volume, of the activated complex and of the reactants A, B, etc., respectively, and E_0 is the difference at the absolute zero between the energy per mole of activated complex and the sum of the energies of the reactants, *i.e.*, the activation energy of the reaction at the absolute zero. The partition functions of the reactants can generally be obtained without difficulty, and the evaluation of F_{\ddagger} for the activated complex can be made provided that the potential-energy surface of the system has been plotted. The position of the activated complex, at the top of the most favorable reaction path, gives the dimensions from which the moments of inertia can be calculated; and by utilizing the theory of small vibrations (page 115), in conjunction with the potential-energy surface, the normal vibration frequencies of the activated complex can be obtained. With this information, it is possible to evaluate the required partition function. Finally, the activation energy at the absolute zero (E_0) can also be obtained from the potential-energy surface, and so all the data are available for the determination of the specific reaction rate by means of Eq. (25). Since the plotting of the potential surface involves the use of spectroscopic data only and F_A , F_B , etc., are also derived from spectral measurements, it is evidently possible, at least in principle, to calculate the absolute rate of a chemical reaction from a knowledge of certain physical properties of the molecules concerned. Even when the potential-energy surface cannot be obtained, it is possible to estimate values of F_{\ddagger} that are not greatly in error, by analogy with a stable molecule of similar structure; in these instances the quantity

$$\left(\frac{kT}{h} \right) \frac{F_{\ddagger}}{F_A F_B \dots}$$

approximately equal to the frequency factor A in the simple rate equation $k = Ae^{-E/RT}$, can be evaluated. The complete statistical theory of absolute reaction rates can thus be used to give both factors, *viz.*, A and E , in terms of which the rate of a reaction can be expressed; but where insufficient information is available for the calculation of the latter, it is often possible to derive the former of these two important quantities.

Comparison of Collision and Statistical Theories.²³—In the collision theory of bimolecular reactions the frequency factor is identified with the quantity PZ in Eq. (7), whereas in the statistical theory just considered it is virtually equivalent to

$$\frac{kT}{h} \frac{F_{\ddagger}}{F_A F_B}$$

The partition function factor $F_{\ddagger}/F_A F_B$ involves certain properties, *e.g.*, masses, of the reactants in the denominator, whereas the collision number Z contains similar quantities in the numerator; it would appear, therefore, that the results of the collision and statistical theories would be incompatible. It must be remembered, however, that the activated complex is made up of the reactants, and so their properties also appear in the numerator of $F_{\ddagger}/F_A F_B$; but, as may be expected, the two methods of treatment do not necessarily lead to the same result.

In comparing the statistical and simple collision methods of approach to the problem of reaction rates, it is instructive to consider first a reaction between two *atoms*, *viz.*, A and B , of masses m_A and m_B and collision diameters σ_A and σ_B ; the collision number Z , for a concentration of one atom of A and one of B per unit volume, is then given by Eq. (5), the mean molecular diameter $\sigma_{A,B}$ being taken as $\frac{1}{2}(\sigma_A + \sigma_B)$. The activated complex for the reaction will be the diatomic molecule AB^{\ddagger} ; this has three degrees of translational freedom and two of rotation, the normal vibrational mode possessed by a diatomic molecule being replaced by translation in the coordinate of decomposition. It follows, therefore, that

$$F_{\ddagger} = \frac{[2\pi(m_A + m_B)kT]^{3/2}}{h^3} \left(\frac{8\pi^2 I kT}{h^2} \right), \quad (26)$$

²³ Eyring, Ref. 21; C. E. H. Bawn, *Trans. Faraday Soc.*, **31**, 1536 (1935); **32**, 178 (1936); C. N. Hinshelwood, *J. Chem. Soc.*, 635 (1937); R. P. Bell, *Ann. Rep. Chem. Soc.*, **36**, 82 (1939).

where the first term on the right-hand side is the partition function for three degrees of translational freedom (page 171) and the second is that for rotation of a diatomic molecule (page 179). The moment of inertia I of the activated complex is given by

$$I = \sigma_{A,B}^2 \frac{m_A m_B}{m_A + m_B} \quad (27)$$

where $\sigma_{A,B}$ has here the precise significance of the distance between the centers of the atoms in the activated state. The atoms A and B have only translational degrees of freedom, and so the respective partition functions are

$$F_A = \frac{(2\pi m_A kT)^{3/2}}{h^3}, \quad (28)$$

and

$$F_B = \frac{(2\pi m_B kT)^{3/2}}{h^3}. \quad (29)$$

It follows, therefore, from Eqs. (26), (28) and (29) and from the statistical equivalent of the frequency factor A, that

$$\frac{kT}{h} \frac{F_{\ddagger}}{F_A F_B} = \sigma_{A,B}^2 \left[8\pi kT \frac{m_A + m_B}{m_A m_B} \right]^{1/2}, \quad (30)$$

which is identical with the collision number given by Eq. (5), as it should be if the statistical and collision treatments lead to the same result. It may be pointed out, however, that the former procedure gives a clear interpretation of the quantity $\sigma_{A,B}$: it is not merely to be regarded as the mean of the collision diameters of the reacting substances; it is determined by the configuration of the activated complex.

The treatment given for two atoms can be extended to reactions involving molecules; but as this becomes complicated, a simplified procedure may be adopted. The approximation will be made, in the first place, of regarding the partition function for each type of energy as consisting of a number of *equal* terms, one for each degree of freedom. Thus, writing f_T , f_R and f_V for the contribution of each translational, rotational and vibrational degree of freedom to the total partition function F , then

$$F = f_T^3 f_R^2 f_V^3, \quad (31)$$

where t , r and v are the numbers of the respective degrees of freedom which contribute. For the reaction between two atoms,

$$F_A = f_T^3, \quad F_B = f_T^3, \quad \text{and} \quad F_{\ddagger} = f_T^3 f_R^2; \quad (32)$$

$$A \approx \frac{kT}{h} \cdot \frac{F_{\ddagger}}{F_A F_B} \approx \frac{kT}{h} \cdot \frac{f_R^2}{f_T^3}, \quad (33)$$

and hence the quantity $(kT/h)f_R^2/f_T^3$ may be regarded as identical with the kinetic-theory collision number Z as shown above. If now the most general case is taken, where A and B are non-linear molecules containing n_A and n_B (both greater than two) atoms respectively,

$$F_A = f_T^3 f_R^3 f_V^{3n_A-6}, \quad (34)$$

$$F_B = f_T^3 f_R^3 f_V^{3n_B-6}, \quad (35)$$

and

$$F_{\ddagger} = f_T^3 f_R^3 f_V^{(n_A+n_B)-7}, \quad (36)$$

the activated complex having one degree of vibrational freedom less than that for a normal molecule with $n_A + n_B$ atoms. It follows, therefore, that if, as an approximation, the respective values of f_T , f_R , and f_V for A, B and the complex are assumed to be the same, then

$$A \approx \frac{kT}{h} \cdot \frac{F_{\ddagger}}{F_A F_B} \approx \frac{kT}{h} \cdot \frac{f_V^5}{f_T^3 f_R^3}. \quad (37)$$

The collision number Z is approximately equivalent to

$$\left(\frac{kT}{h}\right) \left(\frac{f_R^2}{f_T^3}\right)$$

and so in the general case the rates given by the statistical and collision theories differ by a factor $(f_V/f_R)^5$. It has been mentioned (page 6) that in practice the simple collision-theory equation (4) does not hold, and it is necessary to introduce the probability factor P as in Eq. (7): it follows, therefore, according to the statistical theory, that P may be identified approximately with the quantity $(f_V/f_R)^5$: thus

$$P \approx \left(\frac{f_V}{f_R}\right)^5. \quad (38)$$

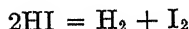
The foregoing calculation was based on the assumption that

both reacting molecules were nonlinear and each contained three or more atoms: a similar computation may be made for reactants of different types, and the results are summarized in Table I.

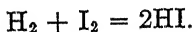
TABLE I.—RELATION BETWEEN TYPES OF REACTANTS AND PROBABILITY FACTOR

Type of Reactant	P
I. Two atoms.....	1
II. An atom and a diatomic molecule:	
a. Nonlinear complex.....	f_v/f_R
b. Linear complex.....	$(f_v/f_R)^2$
III. An atom and a polyatomic molecule.....	$(f_v/f_R)^2$
IV. Two diatomic molecules:	
a. Nonlinear complex.....	$(f_v/f_R)^3$
b. Linear complex.....	$(f_v/f_R)^4$
V. A diatomic and a polyatomic molecule.....	$(f_v/f_R)^4$
VI. Two polyatomic molecules.....	$(f_v/f_R)^5$

Interpretation of the Probability Factor.—The interpretation of the P factors in terms of the vibrational and rotational partition functions leads to some interesting conclusions. At ordinary temperatures, f_v is generally of the order of unity, although if the vibrational frequencies are low, *i.e.*, if the atoms are loosely bound together, it may be higher. The partition function f_R is of the order of 10 to 100, and so f_v/f_R is approximately 10^{-1} to 10^{-2} . In the case of a reaction between polyatomic molecules the probability factor should be about 10^{-5} to 10^{-10} : moreover, the larger the molecule, the larger will be the value of f_R and hence the smaller the P factor. The statistical theory thus accounts for the low values of P observed for many reactions in the gas phase and in solution: such reactions generally involve relatively complex molecules. If one of the reactants is an atom or a diatomic molecule, the probability factor will not be seriously different from unity: for such small molecules, f_R may be less than 10, and hence the quantity $(f_v/f_R)^3$ may be of the order of 10^{-1} or 10^{-2} . This explains why the simple collision theory, with P assumed to be unity, leads to an approximately correct value for the rates of the reactions



and



Processes in which a simple ion, *e.g.*, I^- , OH^- , is one of the reactants also have probability factors close to unity, as may be expected; but it appears that even with relatively complex ions the deviation from the simple collision hypothesis is not always large.

The configuration of the activated complex should, according to Table I, have some influence on the probability factor and hence on the reaction rate. When a linear complex is formed, the rate should be less by a factor of f_V/f_R than for a nonlinear complex, provided that the activation energy is the same in the two cases. If the reactant molecules have to be placed together in a particular way before they can react, the probability of the formation of the activated complex will be less than if there is no restriction, and hence the reaction will be slower in the former instance. There is evidently some correspondence between the P factors arising in this manner and the steric effects postulated by supporters of the collision theory.

A physical picture of the results obtained by the statistical theory may be given in terms of the collision theory of chemical reactions. If the reactants are both polyatomic molecules, the formation of the activated complex is accompanied by the disappearance of three translational and three rotational degrees of freedom, and the formation of five new vibrational degrees of freedom and one of translation along the reaction coordinate. The low probability factor that is found is clearly due to the restrictions on the molecule making the energy transitions involved in the formation of the activated complex. Two molecules possessing the necessary energy for reaction may approach, but unless the energy can be transferred to the appropriate degrees of freedom the activated complex cannot form. The simpler the reacting molecules the smaller is the number of degrees of freedom between which energy transitions must occur, and so the more closely does the probability factor approximate to unity.

It should be mentioned that fundamentally the collision and statistical theories should always give the same results, provided that the former were applied in the proper manner.²⁴ According

²⁴ Cf. Hinshelwood, Ref. 23; Bell, Ref. 23; R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Chap. XII, Oxford University Press, 1939.

to the simple collision theory, the reactants are regarded as rigid bodies with no internal degrees of freedom. But this is true only if the substances concerned are atoms; and, as seen above, in this case the two methods of approach lead to the same conclusion. If adequate allowance could be made in the calculation of the collision number for the fact that the interacting molecules have, in internal degrees of freedom, energy that undergoes changes, the reaction rate would be the same as that obtained by the statistical method; the fact remains, however, that the latter procedure can be employed without great difficulty, whereas no successful attempt has yet been made at a complete collision theory, except in so far as the statistical approach may be regarded as a collision theory.

Entropy of Activation.²⁵—According to Eq. (24) the frequency factor A appears to be equivalent to $(kT/h) e^{\Delta S^\ddagger/R}$, but this is not strictly correct, since ΔH^\ddagger is not equal to the experimental activation energy. It will be shown in Chap. IV (page 199) that if the specific reaction rate is expressed in terms of concentrations it can be represented, for a *bimolecular gas reaction*, by either of the expressions

$$k = e^2 \frac{kT}{h} e^{\Delta S_c^\ddagger/R} e^{-E/RT} \quad (39)$$

and

$$k = e^2 \frac{kT}{h} RT e^{\Delta S_p^\ddagger/R} e^{-E} \quad (40)$$

where ΔS_c^\ddagger and ΔS_p^\ddagger are the entropies of activation with unit concentration or unit pressure, respectively, as the standard states, and E is the experimental activation energy. The frequency factor is thus given by $e^2(kT/h) e^{\Delta S_c^\ddagger/R}$, and it is of interest to see what value the entropy of activation must have in order that the simple collision theory should be obeyed, *i.e.*, for the condition

$$Z = e^2 \frac{kT}{h} e^{\Delta S_c^\ddagger/R} \quad (41)$$

²⁵ Kohnstamm and Scheffer, Ref. 10; Scheffer and Brandsma, Ref. 10; Brandsma, Ref. 10; La Mer, Ref. 11; Wynne-Jones and Eyring, Ref. 21.

or

$$Z = e^2 \frac{kT}{h} RT e^{\Delta S_p^\ddagger/R} \quad (42)$$

to be applicable. If the specific reaction rate is expressed in cc. mole⁻¹ sec.⁻¹ units, so that the standard state is a concentration of 1 mole per cc., Z is of the order of 10^{14} for binary collisions; and since $e^2(kT/h)$ is about 5×10^{13} at ordinary temperatures, it follows that $e^{\Delta S_c^\ddagger/R}$, for this standard state, should have a value of approximately 2. It is evident, therefore, that if the simple collision theory is to be applicable, the entropy of activation, the standard state being a concentration of 1 mole per cc. of gas, should be of the order of 1 cal./deg. per mole, *i.e.*, 1 E.U. per mole. Since the collision number involves the square root of the temperature, whereas the corresponding factor in the theory of absolute reaction rates is directly proportional to the temperature, it is evident that the particular value of ΔS_c^\ddagger which will make the collision theory applicable depends on the temperature; as a rough generalization, however, it may be stated that if ΔS_c^\ddagger has an appreciable positive value the observed reaction rate should be greater than that given by the simple collision hypothesis, whereas if ΔS_c^\ddagger is appreciably negative the rate will be less than calculated from this theory.

It has been seen (page 20) that for a reaction involving two atoms or simple molecules there is a relatively small rearrangement of energy between the various degrees of freedom in the formation of the activated state: in these circumstances, ΔS_c^\ddagger may be expected to be small, and hence the absolute reaction rate and collision theories give results of the same order. On the other hand, when reaction occurs between complex molecules and there is a considerable rearrangement of energy among the degrees of freedom, there is a decrease of entropy in the formation of the activated complex and the reaction rate will be lower than that calculated by the collision hypothesis. These qualitative conclusions may be illustrated by the data in Table II for five reactions of increasing complexity. The separate translational, rotational and vibrational entropies of the reactants and of the activated complexes have been calculated by familiar methods from the appropriate partition functions; the necessary information in the cases of the activated complexes has been obtained

either from the potential-energy surfaces or by making reasonable assumptions concerning the structure of these complexes. The entropies quoted are those generally found in thermodynamic literature, *i.e.*, for a standard state of gas at 1 atm. pressure, and from these the appropriate ΔS_p^\ddagger values have been deduced. In

TABLE II.—COMPARISON OF ENTROPY OF ACTIVATION AND FREQUENCY FACTOR

	Entropy			ΔS_p^\ddagger	ΔS_c^\ddagger	A
	Trans.	Rot.	Vibr.			
$2\text{H} \rightarrow \text{H}_2(300^\circ\text{K.}):^{26}$						
2H.....	52.4	0	0	-14.8	5.3
H_2^\ddagger	28.2	9.4	0			
$2\text{Cl} \rightarrow \text{Cl}_2(300^\circ\text{K.}):^{26}$						
2Cl.....	73.2	0	0	-18.0	2.1
Cl_2^\ddagger	38.7	16.5	0			
$\text{H}_2 + \text{I}_2 = 2\text{HI} (300^\circ\text{K.})^{27}$						
H_2	28.2	2.1	0			
I_2	42.8	17.0	0	-20.3	-0.2	$\sim 10^{14}$
$\text{H}_2\text{I}_2^\ddagger$	42.8	23.1	3.9			
Dimerization of ethylene ($300^\circ\text{K.}):^{28}$						
$2\text{C}_2\text{H}_4$	72.4	31.8	1.32	-30.1	-10.0	$\sim 10^{11}$
$\text{C}_4\text{H}_8^\ddagger$	38.3*	32.7*	4.4*			
Dimerization of butadiene ($600^\circ\text{K.}):^{29}$						
$2\text{C}_4\text{H}_6$	81.2	64.8	31.6	-38.5	-17.0	$\sim 10^{10}$
$\text{C}_8\text{H}_{12}^\ddagger$	43.7	51.4†	44.0			

* Assumed to be the same as 1-butene.

† Includes contribution due to electron multiplicity.

order to obtain ΔS_c^\ddagger , use is made of the fact, which may be derived from Eqs. (41) and (42), that for a *bimolecular gas reaction*

$$\Delta S_c^\ddagger = \Delta S_p^\ddagger + R \ln RT \quad (43)$$

$$= \Delta S_p^\ddagger + R \ln pv. \quad (44)$$

In the present case, p is 1 atm. and v is the volume in cubic centimeters occupied by 1 mole of gas at the temperature T , *i.e.*,

²⁶ H. Eyring, H. Gershinowitz and C. E. Sun, *J. Chem. Phys.*, **3**, 786 (1935).

²⁷ A. Wheeler, B. Topley and H. Eyring, *ibid.*, **4**, 178 (1936).

²⁸ K. S. Pitzer, *ibid.*, **5**, 473 (1937).

²⁹ G. B. Kistiakowsky and W. W. Ransom, *ibid.*, **7**, 725 (1939).

22,412T/273 cc.; hence,

$$\Delta S_e^\ddagger = \Delta S_p^\ddagger + 20.1 \quad (45)$$

at 300°K., the entropies being expressed in cal. deg.⁻¹ mole⁻¹. The results in the column headed ΔS_e^\ddagger were thus obtained by adding 20.1 to the values of ΔS_p^\ddagger at 300°K.; at 600°K. the corresponding difference is 21.5. The experimental frequency factors, which should be about 10^{14} if the simple collision hypothesis is correct, are given in the last column.

In view of the fact that atomic reactions are exceptional, in so far as it is necessary to have a third body to carry off the excess energy produced in the reaction (page 112), it is impossible to make any comparison between ΔS_e^\ddagger and the difference between the expected and actual values of A ; but for the other three reactions the experimental data are in agreement with expectation. The frequency factor has the value required by the simple collision hypothesis only if ΔS_e^\ddagger , for a standard state of 1 mole per cubic centimeter, is zero or has a small positive value: if the entropy of activation has an appreciable negative value, then the reaction is slower than the simple theory requires.

It is of interest to consider briefly the physical significance of the entropy of activation: in view of the relationship between entropy and probability, it is apparent that a negative value of ΔS^\ddagger implies a small probability of the formation of the activated state. An analogous conclusion was reached on page 22 from a consideration of the rearrangement of the energy among the various degrees of freedom that accompanies the formation of the activated complex. The two points of view are, of course, two different aspects of the same fundamental problem: in each case, it is clear that every collision with the requisite amount of energy does not necessarily lead to the formation of the activated complex, and the probability of this formation is an essential factor in determining the rate of the reaction.

It is to be anticipated that in many reactions the activated state will resemble very closely the final state³⁰; if this were so, the entropy of activation ΔS^\ddagger would not differ greatly from the entropy change ΔS accompanying the complete reaction. In many instances, therefore, a parallelism may be expected between $e^{\Delta S^\ddagger/R}$ and the probability factor P of the collision theory: this

³⁰ E.g., I. Welinsky and H. A. Taylor, *ibid.*, 6, 466. (1938).

conclusion was reached, along somewhat different lines, by F. G. Soper,³¹ and the data compiled by him are recorded in Table III. Since the general arguments given above are applicable to reactions in solution, as well as to those in the gas phase, some of the former type are included.

TABLE III.—OVER-ALL ENTROPY CHANGE AND THE PROBABILITY FACTOR

Reaction	P	$e^{\Delta S/R}$
Dimethylaniline + methyl iodide..	0.5×10^{-7}	0.9×10^{-8}
Saponification of ethyl acetate.....	2.0×10^{-6}	5.0×10^{-4}
Chlorination of phenolic ethers....	1.5×10^{-6}	2.2×10^{-5}
Sodium arsenite + tellurate.....	10^{-5}	10^{-11}
Ethylene + hydrogen.....	0.05	10^{-6}
Dissociation of hydrogen iodide....	0.5	0.15
Isomerization of ammonium cyanate	1	0.1
Dissociation of nitrous oxide.....	1	1

The general parallelism between the values of P and $e^{\Delta S/R}$ is very striking; such discrepancies as exist must be due to the incorrectness of the assumption that the activated complex has almost the same entropy as the final state.

Unimolecular Reactions.—The problem of unimolecular reactions is complicated by the fact that few, if any, of those studied are simple processes free from a chain mechanism or other complexity. It appears, however, as mentioned on page 9, that the observed rates are frequently greater than those calculated from the simple collision theory; the difficulty was overcome by the suggestion that several degrees of freedom contribute to the energy of activation. The statistical theory of reaction rates, however, requires no distinction, in this respect, between unimolecular and bimolecular processes. If a molecule ABC undergoes unimolecular decomposition, it will, as the result of acquiring the necessary energy in the proper degrees of freedom in a suitable collision, pass through the activated state ABC^\ddagger , which may not be fundamentally different from the reactant. The only energy transition involved is the change from one vibrational to the new translational degree of freedom along the coordinate of decomposition. The probability of the formation of the activated state, therefore, may well be high; and hence

³¹ F. G. Soper, *J. Chem. Soc.*, 1393 (1935).

the reaction can be more rapid than calculated from the simple collision theory.

The same conclusion may be reached in another manner from a consideration of the appropriate form of Eq. (25). If, as on page 17, the partition functions are assumed, in the first approximation, to be equal to the product of a number of terms that are identical for each type of energy, the rate equation may, in the simplest case, be written as

$$k = \frac{kT}{h} \cdot \frac{f_T^3 f_R^3 f_V^{3n}}{f_T^3 f_R^3 f_V^{3n}} ; e^{-E_0/RT}, \quad (46)$$

the reactant and activated complexes both being taken as non-linear molecules containing n atoms. The translational degrees of freedom are identical in initial and activated states, and those for rotation and vibration will not differ greatly; hence, Eq. (46) may be reduced to

$$k = \frac{kT}{h} \frac{1}{f_V} e^{-E_0/RT} \quad (47)$$

so that the frequency factor is approximately equivalent to $(kT/h)/f_V$. If the value is to be the same as given by the simple collision theory, it should be roughly $(kT/h)f_R^2/f_T^2$, and so that required by the statistical theory is greater by a factor of $f_T^3/f_R^2 f_V$. Since f_T is generally of the order of 10^8 , this quantity may be very large, as is often found to be the case: for reasons given below, however, the discrepancy is not so large as this result would imply.

In general, the activated complex will have a looser structure than the reactant, and hence there will be a greater randomness of motion in the activated state. Its formation will thus be accompanied by an increase of entropy, and, as already seen, an appreciable positive value of ΔS^\ddagger will mean that the reaction rate is greater than required by the simple collision theory.*

It may be pointed out that not all unimolecular reactions have high velocities: this is sometimes due to the fact that the activated complex has a more rigid structure than the initial state (see page 296), and hence ΔS^\ddagger is negative. Another factor, which

* For a unimolecular process the specific reaction rate is independent of the concentration units, *i.e.*, of the standard state, and so ΔS_c^\ddagger and ΔS_p^\ddagger are identical.

results for many unimolecular reactions in lower velocities than would be expected from the simple equations considered above, is that the transmission coefficient (page 13) is appreciably less than unity. This means that the average frequency at which activated complexes pass over the top of the energy barrier *and decompose* will be considerably less than kT/h . The reasons for the possible low transmission coefficients will be considered more fully in Chaps. V and VI.

CHAPTER II

QUANTUM MECHANICS

THE SCHRÖDINGER WAVE EQUATION

Duality of Radiation.—The fact that light can be diffracted suggests that radiation is a wave motion; but, on the other hand, photoelectric phenomena and the Compton effect¹ indicate that radiation is propagated in the form of corpuscles, generally called “photons.” A possible method of resolving the paradox becomes apparent when the means whereby the different properties are detected are considered. If the method of detection involves an object of appreciable size in comparison with the so-called wave length of the radiation, as is the case with a diffraction grating, the undulatory properties are evident, but when the detector is small, *e.g.*, an electron in the Compton effect, the radiation behaves as a stream of particles. This conclusion can be put in another way: if the radiation may be regarded as a stream of photons, then the use of an electron as a measuring device allows the position of the photons to be determined almost exactly. When a ruled grating or thin slit is employed, however, the direction of the photon stream is no longer definite, and the diffraction pattern obtained is an expression of the uncertainty involved. It should be noted, however, that whereas in the Compton experiment the position of the photon can be found, the impact with the electron results in a change of momentum, which means, as will be seen below, that the wave length cannot be measured with any exactness. With a grating, however, the wave length, or momentum, can be obtained accurately but, as seen above, the position of the photon is uncertain. It appears, therefore, that there is, in general, an inverse relationship between the accuracy of measurement of the position and momentum, or wave length, of a photon.

The Uncertainty Principle.²—The same conclusion may be reached for other particles, *e.g.*, electrons, in a somewhat different

¹ A. H. Compton, *Phys. Rev.*, **21**, 483 (1932); **22**, 409 (1923).

² W. Heisenberg, *Z. Physik*, **43**, 172 (1927).

manner. Suppose it is desired to measure the position and momentum of an electron; then assume that a microscope is available in which it can be seen. By illuminating the electron A with light of wave length λ and observing it in the lens B (Fig. 1), the position may be found, according to optical theory, with an accuracy of $\lambda/\sin \theta$, where θ is the aperture of the lens. If x represents a coordinate of position, then the uncertainty Δx of measurement is given by

$$\Delta x = \frac{\lambda}{\sin \theta}. \quad (1)$$

In order to determine the position accurately, Δx should be as small as possible; *i.e.*, λ must be small, and light of short wave length, *e.g.*, γ -rays, should be used. In these circumstances, however, the Compton effect becomes appreciable; the electron undergoes a recoil as a result of impact with the γ -ray photon, and its momentum is thereby changed. A photon behaves as a particle of momentum mc , where c is the velocity of light, and since the mass m and energy E of a particle are connected by the relativity relationship $E = mc^2$, it follows that

$$p = mc = \frac{E}{c}, \quad (2)$$

p being the momentum of the photon. By the quantum theory, $E = h\nu$ where h is Planck's constant and ν is the frequency of the radiation, and since the product of frequency and wave length (λ) gives the velocity of light, it follows from Eq. (2) that

$$p = \frac{h\nu}{\lambda\nu} = \frac{h}{\lambda}. \quad (3)$$

After the impact, however, the scattered photon has a momentum different from h/λ ; but it will still pass through the microscope lens and be brought to a focus, provided that the momentum lies within the range $(1 - \sin \theta)h/\lambda$ and $(1 + \sin \theta)h/\lambda$. It follows, therefore, that the transfer of momentum less than $\pm(\sin \theta)h/\lambda$ from the photon to the electron could not be

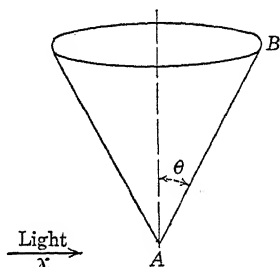


Fig. 1.—Uncertainty of position of an electron.

detected in the microscope; and hence there will be an uncertainty Δp of $(\sin \theta)2h/\lambda$ in the momentum of the electron; i.e.,

$$\Delta p = \frac{(\sin \theta)2h}{\lambda}. \quad (4)$$

The product of the uncertainties of position and momentum is thus given by

$$\Delta x \Delta p = 2h \quad (5)$$

and hence is independent of the wave length of the light. Any attempt to gain accuracy of position, therefore, by the use of light of short wave length, will be offset by a loss of accuracy in the determination of momentum. If the latter is measured accurately, by means of light of long wave length, the position can be obtained only with great uncertainty. The relationship concerning the uncertainty in the determination of conjugate variables, such as position and momentum or energy and time, is quite general, and the product of the two quantities is always approximately of the order of Planck's constant, so that

$$\Delta p \Delta q \approx h. \quad (6)$$

This is the expression of Heisenberg's "uncertainty principle," which has been assumed to be a fundamental law of nature.

Electrons as Waves.—The acceptance of the uncertainty principle means that the old mechanics must be discarded, since it is no longer possible to assign a definite position and momentum to a particle. The discrepancy is not serious for objects of reasonable size, but for small particles, such as electrons, a new mechanics must be used in which a function is employed expressing the *probability* of a particle of given momentum being at a given point, since it is not possible to say that it is *at* the point. The properties of light were explained by Clerk Maxwell on the assumption that the radiations consisted of electromagnetic disturbances obeying the general wave equation

$$\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 w}{\partial z^2} = \frac{1}{c^2} \cdot \frac{\partial^2 w}{\partial t^2}, \quad (7)$$

where x , y and z are coordinates of position, c is the velocity of light, and w is the amplitude of the wave which is a function of x , y and z , and of the time t . This view can be correlated with the

particle properties by saying that the photon is not definitely in any part of the wave, but the probability of finding it at any point is given by the square of the amplitude, *i.e.*, by w^2 , at that point.

Even before the enunciation by Heisenberg of the uncertainty principle, L. de Broglie³ had suggested that electrons behave like photons and are accompanied by waves controlling their motion, just as photons could be regarded as being controlled by electromagnetic waves. In other words, according to de Broglie, an electron beam might be expected, under suitable conditions, to exhibit properties, such as diffraction, that are associated with wave propagation. If the relationship (3) for the momentum, *viz.*, $p = h/\lambda$, deduced for light waves, may be assumed to hold for electrons, then since p is also equal to mv , where m is the mass and v the velocity of the electron, the effective wave length of the electron beam should be given by

$$\lambda = \frac{h}{mv}. \quad (8)$$

These remarkable suggestions were confirmed, shortly after they were put forward, by the work of L. H. Germer and C. Davisson⁴ and of G. P. Thomson:⁵ it was shown that an electron beam could be diffracted and that the apparent wave length obtained from the results was in excellent agreement with that calculated from Eq. (8).

The Wave Equation.—On the assumption that the wave equation for an electron or other small particle is similar to that for a photon, Eq. (7) may be written in the form

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial^2 \Phi}{\partial z^2} = \frac{1}{u^2} \cdot \frac{\partial^2 \Phi}{\partial t^2}, \quad (9)$$

where u is the velocity of propagation of the *electron waves** and Φ is the amplitude: if the latter is real, $\Phi^2 dx dy dz$, abbreviated to $\Phi^2 d\tau$, is the probability of finding an electron in the volume element $dx dy dz$, or $d\tau$, of the configuration space at the time t .

³ L. de Broglie, *Ann. phys.*, [10], **3**, 22 (1925).

⁴ C. Davisson and L. H. Germer, *Phys. Rev.*, **30**, 707 (1927).

⁵ G. P. Thomson, *Nature*, **119**, 890 (1927); *Proc. Roy. Soc.*, **117A**, 600 (1928).

* Sometimes called the phase velocity; it is equal to the velocity of light squared divided by the velocity of the electron.

The velocity u may be replaced by $\lambda\nu$, where ν is the frequency and λ the wave length of the electron waves; and since $p = \hbar/\lambda$, as derived above, and $E = \hbar\nu$ by the quantum theory, it follows that

$$u = \lambda\nu = \frac{E}{p}, \quad (10)$$

and substitution in Eq. (9) gives

$$\frac{\partial^2\Phi}{\partial x^2} + \frac{\partial^2\Phi}{\partial y^2} + \frac{\partial^2\Phi}{\partial z^2} = \frac{p^2}{E^2} \cdot \frac{\partial^2\Phi}{\partial t^2}. \quad (11)$$

If the waves have the form of standing waves, such as those on a string, then Φ must obey the relationship

$$\Phi = \psi(x, y, z)(A \cos 2\pi\nu t + B \sin 2\pi\nu t), \quad (12)$$

where $\psi(x, y, z)$ is a function of x, y and z only, and A and B are constant.* Upon inserting Eq. (12) into (11) the result is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{4\pi^2 p^2}{h^2} \psi, \quad (13)$$

so that t has been eliminated. If V is the potential energy of the particle, then the kinetic energy T is equal to $E - V$: further,

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m}; \quad (14)$$

hence,

$$E - V = \frac{p^2}{2m}, \quad (15)$$

and substitution for p^2 in Eq. (13) gives

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0. \quad (16)$$

This relationship, which, for a single particle, is known as the Schrödinger equation, forms the basis of wave mechanics.⁶

* If either A or B is imaginary, the probability distribution function is $\Phi\bar{\Phi}$ instead of Φ^2 , where $\bar{\Phi}$ is the complex conjugate of Φ . The quantity $\Phi\bar{\Phi}$ and similar products are sometimes written $|\Phi|^2$, where the symbol $|\Phi|$ stands for the "modulus" or "absolute value" of Φ .

⁶ E. Schrödinger, *Ann. Physik*, **79**, 361 (1926); see also *idem, ibid.*, **79**, 489; **80**, 437; **81**, 109 (1926).

ALGEBRA OF OPERATORS

Operator Algebra.—For the further development of the subject, it is desirable to understand the algebra of operators, and hence a short digression will be made for this purpose. If a function u of certain variables is changed into another function v of the same or other variables, by the application of a definite rule, then the process is called an “operation,” represented by

$$\mathbf{F}u = v, \quad (17)$$

where \mathbf{F} is the symbol for the operator, u is the operand and v is the result.* A simple operation, for example, is to multiply a function $f(x)$ of an independent variable x by that variable: then the operator \mathbf{A} is defined by

$$\mathbf{A}f(x) = xf(x). \quad (18)$$

Another operator, *e.g.*, \mathbf{B} , is differentiation with respect to the independent variable, so that

$$\mathbf{B}f(x) = \frac{\partial f(x)}{\partial x}. \quad (19)$$

Operations are not limited to functions of one variable; *e.g.*, a function of two independent variables may be differentiated with respect to one of them. Thus,

$$\mathbf{C}f(x,y) = \frac{\partial f(x,y)}{\partial x}. \quad (20)$$

An important operator is the Laplacian operator ∇^2 called “del squared,” which is represented by

$$\nabla^2 f(x,y,z) = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}. \quad (21)$$

The Schrödinger equation (16) may thus be written in the form

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0. \quad (22)$$

The sum \mathbf{S} of two operators \mathbf{A} and \mathbf{B} is defined by

$$\mathbf{S}f(x) = (\mathbf{A} + \mathbf{B})f(x) = \mathbf{A}f(x) + \mathbf{B}f(x), \quad (23)$$

* Equation (17) should be read “the operation \mathbf{F} applied to the function u gives the function v .”

and the product \mathbf{P} of the same two operators would be given by

$$\mathbf{P}f(x) = \mathbf{A}\mathbf{B}f(x) = \mathbf{A}[\mathbf{B}f(x)]. \quad (24)$$

This means that the function $f(x)$ is first operated on by \mathbf{B} and then \mathbf{A} operates on the result. If \mathbf{A} and \mathbf{B} are as defined by Eqs. (18) and (19) above, then

$$\mathbf{A}\mathbf{B}f(x) = x \frac{\partial f(x)}{\partial x}. \quad (25)$$

If the successive application of two operators produces no change in the operand, then they are said to be reciprocals of each other: they can be represented by \mathbf{A} and \mathbf{A}^{-1} , for example. so that

$$\mathbf{A}\mathbf{A}^{-1} = \mathbf{A}^{-1}\mathbf{A} = \mathbf{I}, \quad (26)$$

where \mathbf{I} is known as the "identity operator." Successive application of the same operator is written \mathbf{A}^n , where n is the number of times \mathbf{A} is applied: for example, if \mathbf{A} is $\partial/\partial x$ then \mathbf{A}^2 is $\partial^2/\partial x^2$, i.e., the second derivative of the function.

It should be noted that the order in which two different operators is applied is of importance: in the case given in Eq. (25), for example, $\mathbf{A}\mathbf{B}f(x)$ is different from $\mathbf{B}\mathbf{A}f(x)$, for the latter is

$$\mathbf{B}\mathbf{A}f(x) = \frac{\partial}{\partial x} [xf(x)] = f(x) + x \frac{\partial f(x)}{\partial x}. \quad (27)$$

If \mathbf{A} and \mathbf{B} were such that $\mathbf{A}\mathbf{B}$ and $\mathbf{B}\mathbf{A}$ are equal, then the operators would be said to "commute": in the illustration given, however, the operators do not commute, and the difference $\mathbf{A}\mathbf{B} - \mathbf{B}\mathbf{A}$ is called the "commutator" of the operators \mathbf{A} and \mathbf{B} .

Linear Operators.—An operator is said to be linear if its application to the sum of two or more operands gives the sum of the results of applying the operator to each operand separately: thus, for a linear operator \mathbf{A} ,

$$\mathbf{A}[f_1(x) + f_2(x)] = \mathbf{A}f_1(x) + \mathbf{A}f_2(x); \quad (28)$$

and if c is an arbitrary constant, real or complex, then

$$\mathbf{A}cf(x) = c\mathbf{A}f(x). \quad (29)$$

Combination of Eqs. (28) and (29) shows that for a linear operator

$$\mathbf{A}[c_1f_1(x) + c_2f_2(x)] = c_1\mathbf{A}f_1(x) + c_2\mathbf{A}f_2(x). \quad (30)$$

If **A** and **B** are linear operators, then it can be readily shown that linear functions of these operators, such as

$$\mathbf{S} = c_1\mathbf{A} + c_2\mathbf{B}, \quad (31)$$

and products, for example,

$$\mathbf{P} = c_3\mathbf{AB}, \quad (32)$$

where c_1, c_2 and c_3 are arbitrary constants, are also linear operators.

An important property of *certain* equations involving linear operators is that any linear combination of separate solutions of the equation is also a solution. Let **A** be a linear operator involving only the same variables, *e.g.*, x_1, x_2, \dots, x_n , as does the operand $f(x_1, x_2, \dots, x_n)$ —abbreviated to $f(x)$ —and suppose the relationship

$$\mathbf{A}f(x) = 0 \quad (33)$$

applies. If $f_1(x)$ and $f_2(x)$, which are also functions of the same variables are solutions of this equation, then

$$\mathbf{A}f_1(x) = 0 \quad \text{and} \quad \mathbf{A}f_2(x) = 0. \quad (34)$$

hence, by Eq. (29) it follows that

$$c_1\mathbf{A}f_1(x) + c_2\mathbf{A}f_2(x) = \mathbf{A}[c_1f_1(x) + c_2f_2(x)] = 0, \quad (35)$$

and so $c_1f_1(x) + c_2f_2(x)$, which is a linear combination of the simple solutions $f_1(x)$ and $f_2(x)$, is also a solution of (33). This general rule can be extended to any number of simple solutions of the original equation.

Hermitian Operators.—If u_1 and u_2 are functions of the variables x_1, \dots, x_n belonging to a definite class, *i.e.*, if the functions satisfy certain specific conditions such as those given below, then an appropriate operator **A** is Hermitian if the following relationship holds:*

$$\int \cdots \int \bar{u}_1 \mathbf{A} u_2 dx_1 \cdots dx_n = \int \cdots \int u_2 \bar{\mathbf{A}} \bar{u}_1 dx_1 \cdots dx_n, \quad (36)$$

or in the abbreviated form

$$\int \bar{u}_1 \mathbf{A} u_2 d\tau = \int u_2 \bar{\mathbf{A}} \bar{u}_1 d\tau, \quad (36a)$$

* To obtain the right-hand side of Eq. (36) from the left-hand the positions of the functions u_1 and u_2 are exchanged, giving $\bar{u}_2 \mathbf{A} u_1$, and then the complex conjugate of the whole is taken.

where the bar over the top of a symbol indicates the complex conjugate.*

The limits of integration depend upon the class of function concerned. In quantum mechanics the functions of particular interest are those which are single-valued and continuous in the complete range of variables, which may include infinity. The squares of the absolute values of the functions, *e.g.*, $|\psi|^2$, must be finite when integrated over the complete range of variables. If ψ is such a function and $\bar{\psi}$ is its complex conjugate, the last condition requires that $\int \psi \bar{\psi} d\tau$, where $d\tau$ represents an element of the configuration space, should be finite. For functions satisfying these conditions, sometimes referred to as "well-behaved functions,"⁷ integration in Eq. (36) or (36a) is carried out over the whole of the configuration space.

It can be shown without difficulty that linear combinations of Hermitian operators are also Hermitian, but this is not necessarily true for the product of such operators. Let **A** and **B** be Hermitian operators suitable for use with a particular class of functions, so that the resulting functions, *e.g.*, $\mathbf{A}u_1$ and $\mathbf{B}u_2$, also belong to this class; then if **B** is considered as the operator and the Hermitian condition of Eq. (36) is used, it is seen that

$$\int (\bar{\mathbf{A}}u_1)\mathbf{B}u_2 d\tau = \int u_2(\bar{\mathbf{B}}\mathbf{A}u_1) d\tau. \quad (37)$$

Taking **A** as the operator, it follows in the same way that

$$\int (\bar{\mathbf{B}}u_2)\mathbf{A}u_1 d\tau = \int u_1(\bar{\mathbf{A}}\mathbf{B}u_2) d\tau. \quad (38)$$

The complex conjugate of the left-hand side of Eq. (37) is

$$\int (\mathbf{A}u_1)(\bar{\mathbf{B}}u_2) d\tau = \int (\bar{\mathbf{B}}u_2)(\mathbf{A}u_1) d\tau, \quad (39)$$

the right-hand side of which is seen to be the same as the left-hand side of Eq. (38), so that the right-hand sides of (37) and (38) must be complex conjugates of each other; *i.e.*,

$$\int u_2(\mathbf{B}\mathbf{A}u_1) d\tau = \int u_1(\bar{\mathbf{A}}\bar{\mathbf{B}}u_2) d\tau. \quad (40)$$

Since no assumption has been made concerning the operators **A** and **B**, except that they are both Hermitian, it follows equally

* If **A** and u are real, then $\bar{\mathbf{A}} = \mathbf{A}$ and $\bar{u} = u$.

⁷ Cf. V. Rojansky, "Introductory Quantum Mechanics," Prentice-Hall, Inc., 1938.

that

$$\int \bar{u}_2(\mathbf{A}B u_1) d\tau = \int u_1(\overline{\mathbf{B}A} \bar{u}_2) d\tau. \quad (41)$$

If the product $\mathbf{A}B$ is to be Hermitian, then

$$\int \bar{u}_2(\mathbf{A}B u_1) d\tau = \int u_1(\overline{\mathbf{A}B} \bar{u}_2) d\tau. \quad (42)$$

Comparison of Eqs. (41) and (42) shows, therefore, that $\mathbf{A}B$ can be Hermitian only if $\mathbf{A}B$ is identical with $\mathbf{B}A$; *i.e.*, the product of two Hermitian operators will itself be Hermitian only if the two operators commute. A special case of commuting operators arises when the two operators are identical: it follows, therefore, that if \mathbf{A} is Hermitian then $\mathbf{A}A$, *i.e.*, \mathbf{A}^2 , is also Hermitian.

Eigenfunctions and Eigenvalues.—If in a given class there are functions $f(x)$ that when operated on by an operator \mathbf{A} are merely multiplied by some constant a , *i.e.*,

$$\mathbf{A}f(x) = af(x), \quad (43)$$

then the members of the class obeying this rule are known as “eigenfunctions” of the operator \mathbf{A} : these eigenfunctions are sometimes said to be the solutions of Eq. (43). The various possible values of a are called the “eigenvalues” of the operator.

If ψ and ϕ are functions belonging to the “well-behaved” class (page 36), and \mathbf{A} is a Hermitian operator, it follows that

$$\int \bar{\phi} \mathbf{A} \psi d\tau = \int \psi (\overline{\mathbf{A} \phi}) d\tau. \quad (44)$$

Further, if the condition of Eq. (43) is satisfied, then

$$\mathbf{A} \psi = a \psi, \quad (45)$$

so that a is an eigenfunction of the operator \mathbf{A} : taking the complex conjugates of the quantities in Eq. (45), the result is

$$\overline{\mathbf{A} \psi} = \bar{a} \bar{\psi}. \quad (46)$$

Multiply both sides of Eq. (45) by $\bar{\psi}$ and both sides of (46) by ψ , and integrate the resulting expressions over the whole of the configuration space in each case, thus

$$\int \bar{\psi} (\mathbf{A} \psi) d\tau = a \int \bar{\psi} \psi d\tau \quad (47)$$

and

$$\int \psi(\bar{A}\psi) d\tau = \bar{a} \int \psi\psi d\tau. \quad (48)$$

If A is Hermitian, the left-hand sides of Eqs. (47) and (48) must be equal; and since $\psi\psi$ and $\bar{\psi}\psi$ are the same, it follows that

$$a = \bar{a}. \quad (49)$$

This can be true only if a is real, so that it follows that for "well-behaved" functions the eigenvalues for Hermitian operators must be real.

POSTULATES OF QUANTUM MECHANICS

General Formulation of Quantum Mechanics.—The next problem is to deduce the fundamental equation of quantum mechanics in a manner different from that already described. Instead of using the wave equation as the basis, certain other postulates will be made. These postulates, like the axioms of geometry, cannot be proved directly; but since many of the conclusions, particularly those relating to the energy levels of hydrogen and helium atoms, have been confirmed by experiment, the postulates may be accepted and the results used in the study of systems involving many particles.

Suppose a system has f degrees of freedom, so that it can be described by f independent dynamical variables, *e.g.*, momenta, p_1, p_2, \dots, p_f , and an equivalent number of independent, dynamically conjugate variables,* *e.g.*, coordinates of position, q_1, q_2, \dots, q_f ; then three postulates are made as follows:

I. Any state of the system is described as fully as possible by a function $\psi(q_1, q_2, \dots, q_f)$ of the "well-behaved" class, such that $\psi\psi dq_1, \dots, dq_f$ is the probability that the variable q_1 has a value between q_1 and $q_1 + dq_1$, that q_2 lies between q_2 and $q_2 + dq_2$, and so on. Since each variable must have some value, the total probability must be unity, so that

$$\int \dots \int \psi\psi dq_1 \dots dq_f = 1 \quad (50)$$

or

$$\int \psi\psi d\tau = 1, \quad (50a)$$

the integral being taken over all possible values of the q 's.

* Dynamically conjugate variables are related to one another by the generalized Hamiltonian equations of motion (see p. 109).

II. To every dynamical variable there corresponds a linear Hermitian operator, which may be obtained by the following rules:

a. If the variable is momentum, *i.e.*, one of the p 's, the operator is

$$\frac{h}{2\pi i} \cdot \frac{\partial}{\partial q}$$

b. If it is a coordinate of position, *i.e.*, one of the q 's, the operation is multiplication by q .*

It will be shown later that these operators for p and q are linear and Hermitian.

c. If it is any other dynamical variable, *e.g.*, energy, expressible in terms of the p 's and q 's, the operator is found by substituting the operator for each p and q in the algebraic expression for the variable, the order of the factors being such as to make the operator Hermitian.

III. If in a given state one of the variables, *e.g.*, the energy, is known to have a value of a precisely, the function ψ is an eigenfunction of the corresponding operator A with the eigenvalue a ; thus,

$$A\psi = a\psi. \quad (51)$$

Such a state is known as an "eigenstate" of the variable.†

To illustrate the application of these postulates, consider a system consisting of a particle, *e.g.*, an electron, of mass m moving in a field of force corresponding to a potential $V(x,y,z)$, which is a function of position. The q 's are chosen as the rectangular coordinates x , y and z of the particle, so that the state of the particle can be described by a function $\psi(x,y,z)$, and the operators for the coordinates x , y and z are then multiplication by x , y and z , respectively. The operators for the conjugate momenta p_x , p_y and p_z in the three directions at right angles are

$$\frac{h}{2\pi i} \frac{\partial}{\partial x}, \quad \frac{h}{2\pi i} \frac{\partial}{\partial y} \quad \text{and} \quad \frac{h}{2\pi i} \frac{\partial}{\partial z},$$

* A mathematically equivalent postulate, which will not be used in this book, is to replace q by the operator $(h/2\pi i)(\partial/\partial p)$ and use multiplication for p .

† When a state is "degenerate" (*cf.* p. 47, footnote), two or more eigenfunctions correspond to the same eigenvalue.

respectively. The Hamiltonian function (H) of a system is an expression of the total energy, *i.e.*, $T + V$, where T is the kinetic and V the potential energy, in terms of the coordinates and momenta. Since T is equal to $p^2/2m$ [Eq. (13)], then if p is treated as a vector quantity the Hamiltonian function can be written in the form*

$$H = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + V(x, y, z), \quad (52)$$

and the corresponding Hamiltonian operator \mathbf{H} , the operator for energy, is therefore, by postulate IIc,

$$\mathbf{H} = \frac{1}{2m} \left[\left(\frac{\hbar}{2\pi i} \cdot \frac{\partial}{\partial x} \right)^2 + \left(\frac{\hbar}{2\pi i} \cdot \frac{\partial}{\partial y} \right)^2 + \left(\frac{\hbar}{2\pi i} \cdot \frac{\partial}{\partial z} \right)^2 \right] + V(x, y, z). \quad (53)$$

If in a given state the total energy is known to be E precisely, then, by postulate III, ψ is a function satisfying the equation

$$\mathbf{H}\psi = E\psi \quad \text{or} \quad \mathbf{H}\psi - E\psi = 0, \quad (54)$$

so that energy states are eigenstates of the Hamiltonian operator. Since this operator is Hermitian, as will be seen shortly (page 43), then according to the deductions on page 37 the energy values must be real.

Upon expanding the expression (53) for \mathbf{H} and inserting in Eq. (54), it is found that

$$\left[-\frac{\hbar^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z) \right] \psi - E\psi = 0, \quad (55)$$

i.e.,

$$\left(-\frac{\hbar^2}{8\pi^2 m} \nabla^2 + V \right) \psi - E\psi = 0. \quad (56)$$

$$\therefore \nabla^2 \psi + \frac{8\pi^2 m}{\hbar^2} (E - V) \psi = 0, \quad (57)$$

which is Schrödinger's equation (page 32). In the case under consideration the three postulates made above lead to the same

* If T had been written as $\frac{1}{2m} \left(\frac{1}{x} p_x^2 x + \frac{1}{y} p_y^2 y + \frac{1}{z} p_z^2 z \right)$, which is algebraically equivalent to the form given in (52), the resulting operator would not be Hermitian; this is because p_x and x , etc., do not commute.

result as do the postulates of page 38. For many purposes, it is convenient to use the form of the Schrödinger equation given in (54), it being understood that the operator \mathbf{H} has the significance indicated in Eq. (53) or, more compactly, as seen from Eq. (56),

$$\mathbf{H} = -\frac{\hbar^2}{8\pi^2m} \nabla^2 + V. \quad (58)$$

For a system of several particles, the Hamiltonian operator is usually written in the form

$$\mathbf{H} = -\frac{\hbar^2}{8\pi^2} \sum \frac{1}{m_i} \nabla_i^2 + V, \quad (59)$$

where m_i is the mass and ∇_i^2 the Laplacian operator for the i th particle, the summation being made for all the particles.

If ψ is the eigenfunction for the Hamiltonian of a system of two electrons, then according to Eqs. (54) and (59) the Schrödinger equation becomes

$$-\frac{\hbar^2}{8\pi^2m} (\nabla_1^2 + \nabla_2^2)\psi + (V - E)\psi = 0, \quad (60)$$

i.e.,

$$(\nabla_1^2 + \nabla_2^2)\psi + \frac{8\pi^2m}{\hbar^2} (E - V)\psi = 0, \quad (61)$$

where

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \quad \text{and} \quad \nabla_2^2 = \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}, \quad (62)$$

x_1, y_1 and z_1 being the coordinates of one electron and x_2, y_2 and z_2 those of the other. If the two electrons are assumed to have no mutual interaction, then the total energy E and the potential V for the combined system may be divided into E_1 and E_2 , and V_1 and V_2 , respectively, the various constituents being the values for the indicated electrons when isolated. It follows, therefore, that under these conditions Eq. (61) may be written

$$\left[\nabla_1^2\psi + \frac{8\pi^2m}{\hbar^2} (E_1 - V_1)\psi \right] + \left[\nabla_2^2\psi + \frac{8\pi^2m}{\hbar^2} (E_2 - V_2)\psi \right] = 0. \quad (63)$$

If ϕ_1 and ϕ_2 are the one-electron eigenfunctions, *i.e.*, the eigenfunctions for the Hamiltonian for each particle alone, then

$$\nabla_1^2 \phi_1 + \frac{8\pi^2 m}{\hbar^2} (E_1 - V_1) \phi_1 = 0 \quad (64)$$

and

$$\nabla_2^2 \phi_2 + \frac{8\pi^2 m}{\hbar^2} (E_2 - V_2) \phi_2 = 0, \quad (65)$$

and from Eqs. (63), (64) and (65) it can be readily shown that

$$\psi = c\phi_1\phi_2, \quad (66)$$

where c is a constant. When there is no interaction between two electrons, the eigenfunction for the system is therefore proportional to the product of the single-electron eigenfunctions. This rule can be extended to a system of any number of electrons. The value of c is generally determined by what is known as the normalizing condition, which will be discussed subsequently.

PROPERTIES OF QUANTUM-MECHANICAL OPERATORS AND FUNCTIONS

Linear and Hermitian Properties of the Operators.—The proof that the operators \mathbf{p} and \mathbf{q} satisfy Eqs. (28) and (29) is simple, and so it is evident that these operators are linear. Since the sums and products of such operators are also linear, it follows that the Hamiltonian operator must be linear.

The operator \mathbf{q} merely involves multiplication by the variable; it is thus clearly Hermitian in character, and the fact that \mathbf{p} is also Hermitian can be shown in the following manner. Suppose ψ and ϕ are two functions belonging to the "well-behaved" class; then consider the integral I involving them, thus,

$$I = \int \cdots \int \psi \mathbf{p}_k \phi \, dq_1 \cdots dq_n, \quad (67)$$

where the integration is carried out over all the possible values of the q 's. Upon inserting the value for the operator \mathbf{p}_k and writing $d\tau$ for $dq_1 \cdots dq_n$, this becomes

$$I = \int \cdots \int \psi \frac{\hbar}{2\pi i} \cdot \frac{\partial \phi}{\partial q_k} \, d\tau, \quad (68)$$

and partial integration with respect to q_k gives

$$I = \int \cdots \int \left(\bar{\psi} \frac{h}{2\pi i} \phi \right)_{q_k = -\infty}^{q_k = +\infty} d\tau' - \int \cdots \int \phi \frac{h}{2\pi i} \cdot \frac{\partial \bar{\psi}}{\partial q_k} d\tau, \quad (69)$$

where $d\tau'$ does not include dq_k . The "well-behaved" functions are single-valued and continuous over the complete range of variables, and so $\int \cdots \int \psi \bar{\psi} d\tau$ and $\int \cdots \int \phi \bar{\phi} d\tau$ must be finite (page 36). These conditions can be satisfied only when ψ and ϕ become zero at $+\infty$ and $-\infty$. It is evident, therefore, that for "well-behaved" functions the left-hand integral of (69) is zero, and hence the expression reduces to

$$= \int \cdots \int \phi \left(-\frac{h}{2\pi i} \cdot \frac{\partial \bar{\psi}}{\partial q_k} \right) d\tau. \quad (70)$$

The complex conjugate of the operator \mathbf{p}_k , i.e., $\bar{\mathbf{p}}_k$, is $-\frac{h}{2\pi i} \cdot \frac{\partial}{\partial q_k}$, and so it is evident that Eq. (70) may be written

$$I = \int \cdots \int \phi \bar{\mathbf{p}}_k \bar{\psi} d\tau \quad \text{or} \quad \int \cdots \int \phi \bar{\mathbf{p}}_k \bar{\psi} dq_1 \cdots dq_n. \quad (71)$$

Comparison of Eqs. (67) and (71) shows at once that \mathbf{p}_k must be Hermitian. It has been seen that the square of a Hermitian operator and the sum of two or more such operators is also Hermitian; it is clear, therefore, that the Hamiltonian operator, since it involves the sum of terms of the type of \mathbf{p}_k^2 and real constants, must also be Hermitian (see page 35). Since the Hamiltonian does not involve i , the operator and its complex conjugate are identical. It is therefore possible to write

$$\int \bar{\phi} \mathbf{H} \psi d\tau = \int \psi \mathbf{H} \bar{\phi} d\tau \quad (72)$$

and

$$\int \bar{\psi} \mathbf{H} \psi d\tau = \int \psi \mathbf{H} \bar{\psi} d\tau. \quad (73)$$

The importance of \mathbf{H} being Hermitian lies in the fact that according to the arguments on page 37 the eigenvalues for the energy E in (54) must always be real.

Normalization and Orthogonality.—If two functions $f_1(x)$ and $f_2(x)$ have the property that

$$\int_a^b \overline{f_1(x)} f_2(x) dx = 0 \quad (74)$$

for a certain interval a, b , the functions are said to be “orthogonal” in that interval. A set of functions $f_1(x), f_2(x), \dots, f_i(x)$, such that any two are orthogonal in the interval a, b , is called an “orthogonal set” in that interval.

If the condition

$$\int_a^b \overline{f_i(x)} f_i(x) dx = 1 \quad (75)$$

holds, where $f_i(x)$ represents any function of x , then the function is said to be “normalized.” If both conditions (74) and (75) are applicable, the whole set of functions are normalized and mutually orthogonal in the interval a, b . In quantum mechanics, where the functions of the “well-behaved” class are of special interest, the interval extends over the whole of the configuration space, so that the condition for normalization is often written

$$\int \overline{\psi} \psi d\tau = 1, \quad (76)$$

and for orthogonality

$$\int \overline{\psi} \psi_j d\tau = 0. \quad (77)$$

An important property of normalized, orthogonal functions is that certain arbitrary functions, *e.g.*, those of the “well-behaved” class, can be expanded into a series of orthogonal functions. For example, if $f(x)$ is any function that can be expanded as a series of orthogonal functions in a given interval a, b , then

$$f(x) = c_1 \phi_1 + c_2 \phi_2 + \dots + c_i \phi_i + \dots \quad (78)$$

where the coefficients $c_1, c_2, \dots, c_i, \dots$ are constants and $\phi_1, \phi_2, \dots, \phi_i, \dots$ are mutually orthogonal functions of the variable x . Upon multiplying both sides of Eq. (78) by $\overline{\phi_i}$ and integrating over the limits of the interval, the result is

$$\begin{aligned} \overline{\phi_i} f(x) dx &= c_1 \int_a^b \overline{\phi_i} \phi_1 dx + c_2 \int_a^b \overline{\phi_i} \phi_2 dx + \dots \\ &\quad + c_i \int_a^b \overline{\phi_i} \phi_i dx + \dots \end{aligned} \quad (79)$$

Since the ϕ 's are orthogonal, all the integrals vanish except the one involving ϕ_i , and this particular one is equal to unity if the functions are normalized: it follows, therefore that

$$c_i = \int_a^b \bar{\phi}_i f(x) dx, \quad (80)$$

and hence the coefficients $c_1, c_2, \dots, c_i, \dots$ can be found if the expansion is valid. The result may, for convenience, be written in another form: if the normalized orthogonal functions $\psi_1, \psi_2, \dots, \psi_i, \dots$ are eigenfunctions of a given operator, such as are encountered in quantum mechanics, the eigenfunction Ψ for any state may be expanded in terms of the ψ 's, thus,

$$\Psi = \sum_i c_i \psi_i, \quad (81)$$

which is the analogue of (78), where

$$c_i = \int \bar{\psi}_i \Psi d\tau \quad (82)$$

by Eq. (80). In general, $d\tau$ is to be taken as an element of the configuration space and integration carried out over the whole of this space.

If Ψ is an eigenfunction that can be expressed in terms of a normalized orthogonal set and $\bar{\Psi}$ is its complex conjugate, then

$$\Psi = c_1 \psi_1 + c_2 \psi_2 + \dots \quad (83)$$

and

$$\bar{\Psi} = \bar{c}_1 \bar{\psi}_1 + \bar{c}_2 \bar{\psi}_2 + \dots \quad (84)$$

If Ψ is normalized,

$$\begin{aligned} \int \Psi \bar{\Psi} d\tau &= \int (c_1 \psi_1 + c_2 \psi_2 + \dots)(\bar{c}_1 \bar{\psi}_1 + \bar{c}_2 \bar{\psi}_2 + \dots) d\tau \\ &= 1. \end{aligned} \quad (85)$$

All terms of the type $\int \psi_i \bar{\psi}_j d\tau$ are zero when $i \neq j$, on account of orthogonality, and unity when $i = j$, because the functions are normalized: hence, it follows that

$$c_1 \bar{c}_1 + c_2 \bar{c}_2 + \dots + c_i \bar{c}_i + \dots = 1, \quad (86)$$

i.e.,

$$\sum_i c_i \bar{c}_i = 1, \quad (86a)$$

which may be regarded as the condition that the eigenfunction Ψ is normalized.

It can be proved that the eigenfunctions of any Hermitian operator are orthogonal functions in the interval corresponding to the complete range of the variables, *e.g.*, over the whole of configuration space. Suppose ψ_1 and ψ_2 are eigenfunctions of the operator \mathbf{A} , and the corresponding eigenvalues are a_1 and a_2 ; then

$$(1) \mathbf{A}\psi_1 = a_1\psi_1 \quad \text{and} \quad (2) \mathbf{A}\psi_2 = a_2\psi_2. \quad (87)$$

Multiply both sides of (1) by $\bar{\psi}_2$, and integrate over the whole of the configuration space; then

$$\int \bar{\psi}_2 \mathbf{A}\psi_1 d\tau = a_1 \int \bar{\psi}_2 \psi_1 d\tau. \quad (88)$$

Further, since \mathbf{A} is Hermitian,

$$\int \bar{\psi}_2 \mathbf{A}\psi_1 d\tau = \int \psi_1 \bar{\mathbf{A}}\bar{\psi}_2 d\tau = a_1 \int \bar{\psi}_2 \psi_1 d\tau. \quad (89)$$

By taking the complex conjugates of both sides of Eq. (87, 2), multiplying by ψ_1 , integrating and making use of the fact that the operator is Hermitian, it is found that

$$\int \bar{\psi}_2 \mathbf{A}\psi_1 d\tau = \bar{a}_2 \int \psi_1 \bar{\psi}_2 d\tau. \quad (90)$$

Since, as shown above, the eigenvalue for a Hermitian operator must be real, *i.e.*, $\bar{a}_2 = a_2$, Eq. (90) becomes

$$\int \bar{\psi}_2 \mathbf{A}\psi_1 d\tau = a_2 \int \psi_1 \bar{\psi}_2 d\tau, \quad (91)$$

and comparison of Eqs. (89) and (91) gives

$$a_1 \int \bar{\psi}_2 \psi_1 d\tau = a_2 \int \psi_1 \bar{\psi}_2 d\tau. \quad (92)$$

If $a_1 \neq a_2$, it follows that

$$\int \bar{\psi}_2 \psi_1 d\tau = 0. \quad (93)$$

Hence the eigenfunctions corresponding to different eigenvalues of the same Hermitian operator are orthogonal. This holds, of course, for the Hamiltonian operator, so that the eigenfunctions ψ which are solutions of the Schrödinger equation $\mathbf{H}\psi = E\psi$, form an orthogonal set.

When two or more independent eigenfunctions correspond to the same eigenvalue, *i.e.*, when the state is "degenerate,"* the arguments concerning orthogonality require some modification. The eigenfunctions corresponding to one particular eigenvalue will be orthogonal to the functions corresponding to another eigenvalue, but those belonging to a particular eigenvalue are not necessarily mutually orthogonal. If required, however, they can be orthogonalized without difficulty. Suppose the two degenerate normalized eigenfunctions ψ_1 and ψ_2 of the linear operator \mathbf{A} correspond to the same eigenvalue a ; then

$$\mathbf{A}\psi_1 = a\psi_1 \quad \text{and} \quad \mathbf{A}\psi_2 = a\psi_2, \quad (94)$$

where ψ_1 and ψ_2 are not orthogonal. If ψ'_2 is defined as $\psi_2 - b\psi_1$, then it can be readily shown that ψ'_2 is also a correct solution; but if ψ_1 and ψ'_2 are to be mutually orthogonal, it is necessary that

$$\begin{aligned} \int \bar{\psi}_1 \psi'_2 d\tau &= \int \bar{\psi}_1 (\psi_2 - b\psi_1) d\tau \\ &= \int \bar{\psi}_1 \psi_2 d\tau - b \int \bar{\psi}_1 \psi_1 d\tau = 0. \end{aligned} \quad (95)$$

Since ψ_1 is normalized, $\int \bar{\psi}_1 \psi_1 d\tau$ is equal to unity, and so the condition for orthogonality is

$$b = \int \bar{\psi}_1 \psi_2 d\tau. \quad (95a)$$

Although ψ_1 and ψ_2 are not orthogonal, therefore, it is possible to find a linear combination of them that does satisfy this requirement.

Matrices.—An important form of the expansion (81) arises when a function ψ is formed by operating on an eigenfunction ϕ_i of one operator by the operator of another variable, *e.g.*,

$$\psi = \mathbf{A}\phi_i, \quad (96)$$

where by Eq. (81)

$$\psi = \sum_i c_i \phi_i. \quad (97)$$

In this particular case the coefficient c_i , which according to Eq. (82) is equal to $\int \bar{\phi}_i \psi d\tau$, is, by (96), $\int \bar{\phi}_i \mathbf{A}\phi_i d\tau$. This quantity

* An energy level or state is said to be "*n*-fold" degenerate when there are *n* linearly independent eigenfunctions that are solutions of the Schrödinger equation with the same eigenvalue (see p. 39).

is represented by the symbol A_{ij} , using the same letter as for the operator; *e.g.*,

$$c_i = \int \bar{\phi}_i \mathbf{A} \phi_j d\tau \equiv A_{ij}. \quad (98)$$

$$\therefore \psi = \sum_i c_i \phi_i = \sum_i A_{ij} \phi_j \quad (99)$$

$$= A_{1j} \phi_1 + A_{2j} \phi_2 + \dots + A_{nj} \phi_n. \quad (99a)$$

The set of quantities A_{ij} found by expanding all the functions in the manner of (99a) is called the "matrix" of the operator \mathbf{A} . It is usually written in the form of a square array* as shown below.

$$\begin{array}{cccc} A_{11} & A_{12} & A_{13} & A_{1n} \\ A_{21} & A_{22} & A_{23} & A_{2n} \\ A_{31} & A_{32} & A_{33} & A_{3n} \end{array}$$

$$A_{n1} \quad A_{n2} \quad A_{n3} \quad A_{nn}.$$

Any particular value A_{ij} is called a "matrix component" or "matrix element" of the operator \mathbf{A} between the eigenfunctions ϕ_i and ϕ_j ; for $i = j$, the component is referred to as a "diagonal element," *e.g.*, A_{11} , A_{22} , etc.

If the operator \mathbf{A} is Hermitian, then

$$A_{ij} = \int \phi_i \mathbf{A} \phi_j d\tau = \int \phi_j \bar{\mathbf{A}} \phi_i d\tau = \bar{A}_{ji}. \quad (100)$$

In a Hermitian matrix, therefore, components that are symmetrical about the diagonal are complex conjugates of each other. If the operator does not contain i , as is the case with the Hamiltonian when terms involving magnetic interaction are negligible, and the eigenfunctions ϕ_i and ϕ_j are real, \bar{A}_{ji} is equal to A_{ji} , so that in this special case $A_{ij} = A_{ji}$.

ANGULAR MOMENTUM AND SPIN OPERATORS

Angular Momenta.—Operators connected with angular momenta are of importance in quantum mechanics. Although

* The array constituting a matrix should not be confused with a determinant, although a matrix often forms part of a determinant, as, for example, on p. 66.

the subject will be developed in a general manner, the results will be applied here to spin angular momentum only. The angular momentum M of a single particle of mass m moving with a velocity v at a distance r from the origin, is given by $m\mathbf{r} \times \mathbf{v}$, where \mathbf{r} and \mathbf{v} are vectors. It can then be shown that the three components of angular momentum M_x , M_y and M_z , about the origin, are defined by

$$M_x = yp_z - zp_y, \quad (101)$$

$$M_y = zp_x - xp_z, \quad (102)$$

$$M_z = xp_y - yp_x, \quad (103)$$

where x , y and z are the coordinates and p_x , p_y and p_z are the corresponding components of the linear momentum. Upon replacing the coordinates and momenta in Eqs. (101), (102) and (103) by the appropriate quantum-mechanical operators (page 39) and taking the order of the factors so as to make the results Hermitian, as required by postulate IIc (page 39), it follows that the operators for angular momenta are

$$\mathbf{M}_x = \frac{\hbar}{2\pi i} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \quad (104)$$

$$\mathbf{M}_y = \frac{\hbar}{2\pi i} \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \quad (105)$$

and

$$\mathbf{M}_z = \frac{\hbar}{2\pi i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \quad (106)$$

These operators do not commute, and upon inserting the actual values from Eqs. (104), (105) and (106) the various commutators are found to be

$$\mathbf{M}_x \mathbf{M}_y - \mathbf{M}_y \mathbf{M}_x = \frac{i\hbar}{2\pi} \mathbf{M}_z, \quad (107)$$

$$\mathbf{M}_y \mathbf{M}_z - \mathbf{M}_z \mathbf{M}_y = \frac{i\hbar}{2\pi} \mathbf{M}_x, \quad (108)$$

and

$$\mathbf{M}_z \mathbf{M}_x - \mathbf{M}_x \mathbf{M}_z = \frac{i\hbar}{2\pi} \mathbf{M}_y. \quad (109)$$

The total angular momentum M is related to the components by

the equation

$$M^2 = M_x^2 + M_y^2 + M_z^2 \quad (110)$$

or, in the operator form,

$$\mathbf{M}^2 = \mathbf{M}_x^2 + \mathbf{M}_y^2 + \mathbf{M}_z^2. \quad (111)$$

The product of the operators $\mathbf{M}_x - i\mathbf{M}_y$ and $\mathbf{M}_x + i\mathbf{M}_y$ can be expanded, thus,

$$(\mathbf{M}_x - i\mathbf{M}_y)(\mathbf{M}_x + i\mathbf{M}_y) = \mathbf{M}_x^2 + i(\mathbf{M}_x\mathbf{M}_y - \mathbf{M}_y\mathbf{M}_x) + \mathbf{M}_y^2; \quad (112)$$

and hence from Eqs. (107), (111) and (112) it follows that

$$\mathbf{M} = (\mathbf{M}_x - i\mathbf{M}_y)(\mathbf{M}_x + i\mathbf{M}_y) + \frac{h}{2\pi} \mathbf{M}_z + \mathbf{M}_z^2. \quad (113)$$

By employing the same methods as were used in investigating the nature of \mathbf{p} and \mathbf{q} , it can be shown that \mathbf{M}_x , \mathbf{M}_y and \mathbf{M}_z are linear and Hermitian.

Electron Spin.—In order to account for certain fine structures in atomic spectra, G. E. Uhlenbeck and S. Goudsmit⁸ suggested that an electron has an intrinsic angular momentum which is equivalent to spin. To satisfy the experimental data, it is necessary to postulate that the square of the total angular momentum of spin expressed in the usual form for angular momentum, *viz.*,

$$M^2 = l(l+1) \left(\frac{h}{2\pi} \right)^2,$$

is $\frac{1}{2}(\frac{1}{2} + 1)(h/2\pi)^2$, so that the component parallel to any given axis can have only the values

$$+\frac{1}{2} \cdot \frac{h}{2\pi} \quad \text{or} \quad -\frac{1}{2} \cdot \frac{h}{2\pi}.$$

Since the quantum numbers of an electron are usually expressed in $h/2\pi$ units, it follows that the so-called "spin quantum numbers" of an electron can be only $+\frac{1}{2}$ or $-\frac{1}{2}$.

Spin Operators.—On the assumption that the spin angular momentum is analogous to the angular momentum considered above, W. Pauli introduced spin operators \mathbf{S}_x , \mathbf{S}_y and \mathbf{S}_z

⁸ G. E. Uhlenbeck and S. Goudsmit, *Naturwissenschaften*, **13**, 953 (1925); *Nature*, **117**, 264 (1926).

corresponding to the three components of spin S_x , S_y and S_z , parallel to the x -, y - and z -axes, respectively. The total spin momentum is related to the components by the usual formula

$$S^2 = S_x^2 + S_y^2 + S_z^2,$$

and the corresponding operator is given by

$$\mathbf{S}^2 = \mathbf{S}_x^2 + \mathbf{S}_y^2 + \mathbf{S}_z^2. \quad (114)$$

It is possible to determine precisely only one of the three components of the spin angular momentum at a time, and by convention this is taken as the one parallel to the z -axis; *i.e.*, the z -component of the spin momentum can have the values of $+\hbar/4\pi$ and $-\hbar/4\pi$ only.

Suppose α and β are the eigenfunctions of the operator \mathbf{S}_z , when the spin quantum numbers are $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively: by the foregoing postulates the corresponding eigenvalues must be $+\frac{1}{2}\hbar/2\pi$ and $-\frac{1}{2}\hbar/2\pi$, respectively. It follows, therefore, that

$$\mathbf{S}_z\alpha = +\frac{1}{2}\left(\frac{\hbar}{2\pi}\right)\alpha \quad (115)$$

and

$$\mathbf{S}_z\beta = -\frac{1}{2}\left(\frac{\hbar}{2\pi}\right)\beta \quad (116)$$

Further, since the square of the total spin momentum, as seen above, is given by

$$S^2 = \frac{1}{2}\left(\frac{1}{2} + 1\right)\left(\frac{\hbar}{2\pi}\right)^2, \quad (117)$$

it follows that

$$\mathbf{S}^2\alpha = \frac{3}{4}\left(\frac{\hbar}{2\pi}\right)^2\alpha \quad \text{and} \quad \mathbf{S}^2\beta = \frac{3}{4}\left(\frac{\hbar}{2\pi}\right)^2\beta. \quad (118)$$

Consider the operator $\mathbf{S}_z(\mathbf{S}_x - i\mathbf{S}_y)$ acting on the eigenfunction α ; upon multiplying out, it is seen that

$$\mathbf{S}_z(\mathbf{S}_x - i\mathbf{S}_y)\alpha = (\mathbf{S}_z\mathbf{S}_x - i\mathbf{S}_z\mathbf{S}_y)\alpha. \quad (119)$$

If the commutation rules derived for the operators of angular momenta may be assumed to apply to spin momenta, then, by

analogy with Eqs. (107), (108) and (109),

$$S_x S_y - S_y S_x = \frac{i\hbar}{2\pi} S_z, \quad (120a)$$

$$S_y S_z - S_z S_y = \frac{i\hbar}{2\pi} S_x, \quad (120b)$$

$$S_z S_x - S_x S_z = \frac{i\hbar}{2\pi} S_y. \quad (120c)$$

Substitution for $S_x S_x$ and $S_x S_y$ from Eqs. (120c) and (120b) in (119) gives

$$S_z(S_x - iS_y)\alpha = \left(\frac{i\hbar}{2\pi} S_y + S_x S_z - \frac{\hbar}{2\pi} S_x - iS_y S_z \right) \alpha \quad (121)$$

$$= (S_x - iS_y)S_z\alpha - \frac{\hbar}{2\pi} (S_x - iS_y)\alpha. \quad (122)$$

Upon replacing $S_z\alpha$ by $(\hbar/4\pi)\alpha$, according to Eq. (115), then

$$S_z(S_x - iS_y)\alpha = \frac{\hbar}{4\pi} (S_x - iS_y)\alpha - \frac{\hbar}{2\pi} (S_x - iS_y)\alpha, \quad (123)$$

$$\therefore S_z[(S_x - iS_y)\alpha] = -\frac{\hbar}{4\pi} [(S_x - iS_y)\alpha]. \quad (124)$$

It is seen that $[(S_x - iS_y)\alpha]$ is an eigenfunction of S_z , and comparison of Eq. (124) with (116) shows that

$$(S_x - iS_y)\alpha = c\beta, \quad (125)$$

where c is a constant; the value of the latter has now to be determined. If the spin eigenfunctions α and β are chosen so as to be normalized, *i.e.*,

$$\int \alpha \bar{\alpha} d\omega = 1 \quad \text{and} \quad \int \beta \bar{\beta} d\omega = 1, \quad (126)$$

then

$$\int (c\beta)(\bar{c}\bar{\beta}) d\omega = c\bar{c}, \quad (127)$$

integration being carried out over the spin coordinates ω .

According to Eq. (125) the function $c\beta$ is equal to $(S_x - iS_y)\alpha$; and the complex conjugate of this, *viz.*, $\bar{c}\bar{\beta}$, is $(\bar{S}_x + i\bar{S}_y)\bar{\alpha}$ or $(\bar{S}_x\bar{\alpha} + i\bar{S}_y\bar{\alpha})$. Hence, by Eq. (127),

$$c\bar{c} = \int (S_x - iS_y)\alpha(\bar{S}_x\bar{\alpha}) d\omega + \int (S_x - iS_y)\alpha i(\bar{S}_y\bar{\alpha}) d\omega. \quad (128)$$

In this expression, \bar{S}_x and \bar{S}_y may be treated as operators in the first and second integrals, respectively; and since, by analogy with \mathbf{M}_x and \mathbf{M}_y , they are Hermitian, it follows that

$$c\bar{c} = \int \bar{\alpha} S_x (S_x - iS_y) \alpha d\omega + \int \bar{\alpha} iS_y (S_x - iS_y) \alpha d\omega \quad (129)$$

$$= \int \bar{\alpha} (S_x + iS_y) (S_x - iS_y) \alpha d\omega \quad (130)$$

$$= \int \bar{\alpha} (S_x^2 + S_y^2 - iS_x S_y + iS_y S_x) \alpha d\omega. \quad (131)$$

From Eq. (114), $S_x^2 + S_y^2 = S^2 - S_z^2$; from (120a),

$$-iS_x S_y + iS_y S_x = \left(\frac{h}{2\pi}\right) S_z;$$

and so Eq. (131) becomes

$$c\bar{c} = \int \bar{\alpha} \left(S^2 - S_z^2 + \frac{h}{2\pi} S_z \right) \alpha d\omega. \quad (132)$$

From Eq. (118), $S^2\alpha$ is equal to $\frac{3}{4}(h/2\pi)^2\alpha$; from (115), $S_z^2\alpha$ is $\frac{1}{4}(h/2\pi)^2\alpha$, whereas $S_z\alpha$ is $\frac{1}{2}(h/2\pi)\alpha$; hence, Eq. (132) reduces to

$$c\bar{c} = \int \bar{\alpha} \left(\frac{h}{2\pi}\right)^2 \left(\frac{3}{4} - \frac{1}{4} + \frac{1}{2}\right) \alpha d\omega, \quad (133)$$

$$= \int \bar{\alpha} \left(\frac{h}{2\pi}\right)^2 \alpha d\omega = \left(\frac{h}{2\pi}\right)^2 \int \bar{\alpha} \alpha d\omega. \quad (134)$$

According to Eq. (126), the integral of $\bar{\alpha} \alpha d\omega$ is unity, the spin eigenfunctions being normalized, and hence

$$c\bar{c} = \left(\frac{h}{2\pi}\right)^2; \quad (135)$$

$$\therefore c = \bar{c} = \frac{h}{2\pi}, \quad (136)$$

and so Eq. (125) may be written

$$(S_x - iS_y)\alpha = \frac{h}{2\pi} \beta. \quad (137)$$

* An alternative solution is $c = \bar{c} = -h/2\pi$; this choice, although not the conventional one, leads to equivalent results.

By an exactly similar argument, it can be shown that

$$(\mathbf{S}_x - i\mathbf{S}_y)\beta = 0, \quad (138)$$

$$(\mathbf{S}_x + i\mathbf{S}_y)\alpha = 0, \quad (139)$$

and

$$(\mathbf{S}_x + i\mathbf{S}_y)\beta = \left(\frac{\hbar}{2\pi}\right)\alpha. \quad (140)$$

By addition and subtraction, it follows from these four equations, (137) to (140), that

$$\mathbf{S}_x\alpha = \left(\frac{\hbar}{4\pi}\right)\beta, \quad \mathbf{S}_x\beta = \left(\frac{\hbar}{4\pi}\right)\alpha; \quad (141)$$

and

$$\mathbf{S}_y\alpha = \left(\frac{i\hbar}{4\pi}\right)\beta, \quad \mathbf{S}_y\beta = -\left(\frac{i\hbar}{4\pi}\right)\alpha. \quad (142)$$

The equation with spin operators corresponding to (113) is

$$\mathbf{S}^2 = (\mathbf{S}_x - i\mathbf{S}_y)(\mathbf{S}_x + i\mathbf{S}_y) + \frac{\hbar^2}{2\pi} \mathbf{S}_z + \mathbf{S}_z^2; \quad (143)$$

and since the results of operating with $(\mathbf{S}_x + i\mathbf{S}_y)$ and $(\mathbf{S}_x - i\mathbf{S}_y)$ on α and β are known from Eqs. (137), (138), (139) and (140), it is a relatively simple matter to determine whether a particular function involving spin is an eigenfunction of both \mathbf{S}^2 and \mathbf{S}_z . The importance of this will be seen later.

Since spin operators, like the corresponding operators for angular momentum, are linear as well as Hermitian, it follows that for a system consisting of several electrons, whose spin function is the product of the spin functions of the various electrons,

$$\begin{aligned} \mathbf{S}_x\phi &= (\mathbf{S}_{x_1} + \mathbf{S}_{x_2} + \mathbf{S}_{x_3} + \cdots)\phi \\ &= \mathbf{S}_{x_1}\phi + \mathbf{S}_{x_2}\phi + \mathbf{S}_{x_3}\phi + \cdots,^* \end{aligned} \quad (144)$$

where \mathbf{S}_{x_1} , \mathbf{S}_{x_2} , \mathbf{S}_{x_3} , etc., are the operators corresponding to the x -components of the spin angular momenta for the constituent

* The use of the symbol \mathbf{S}_x or \mathbf{S}_y , without further subscript, means that the operator applies to *all* the electrons in the system, whether there be one or many; symbols such as \mathbf{S}_{x_1} , \mathbf{S}_{x_2} , \mathbf{S}_{y_1} , \mathbf{S}_{y_2} , etc., imply that the operator refers only to the electron designated by 1, 2, etc.

electrons 1, 2, 3, etc., respectively. Similarly, for any combination of component spin operators, thus

$$\begin{aligned} (\mathbf{S}_x + i\mathbf{S}_y)\phi &= [(\mathbf{S}_{x_1} + i\mathbf{S}_{y_1}) + (\mathbf{S}_{x_2} + i\mathbf{S}_{y_2}) + (\mathbf{S}_{x_3} + i\mathbf{S}_{y_3}) \\ &\quad + \dots]\phi \\ &= (\mathbf{S}_{x_1} + i\mathbf{S}_{y_1})\phi + (\mathbf{S}_{x_2} + i\mathbf{S}_{y_2})\phi + (\mathbf{S}_{x_3} + i\mathbf{S}_{y_3})\phi \\ &\quad + \dots \quad (145) \end{aligned}$$

The result of such a spin operator acting on the total spin function of a system of several electrons is thus the sum of the values obtained by operating in turn on this function by the corresponding operator for each separate electron constituting the system.

EIGENFUNCTIONS FOR ONE OR MORE ELECTRONS

Complete Electron Eigenfunctions.—The complete eigenfunction of an electron must include the spin contribution, and a satisfactory solution is to take the product of the positional eigenfunction, sometimes called an orbital, and the spin eigenfunction. The orbital is the eigenfunction of the Hamiltonian (energy) operator; and since the latter depends only slightly on the magnetic interaction between spin and orbital angular momentum, the separation of the complete eigenfunction into a product of two parts is justifiable. For any positional eigenfunction, a , which depends on the quantum numbers, n , l and m only,* there are two possible spin eigenfunctions, *viz.*, α and β , so that the complete functions may be $a\alpha$ or $a\beta$.

Consider a system of two electrons 1 and 2, for which there are only two positions available; *i.e.*, there are only two orbitals, a and b , that are possible. The single-electron eigenfunctions can be $a\alpha$, $a\beta$, $b\alpha$ and $b\beta$; and if there is no interaction between the electrons, the complete eigenfunction for the system may be the product of either $a\alpha$ or $a\beta$ by $b\alpha$ or $b\beta$ (see page 42). Products such as $(a\alpha)(a\beta)$ and $(b\alpha)(b\beta)$ are neglected because these would mean that both electrons occupy the same orbital, *viz.*, a in the former case and b in the latter, and the corresponding states would be polar.† One of the possible eigenfunctions is

* The numbers n , l and m refer to the so-called total, azimuthal and magnetic quantum numbers, respectively.

† This corresponds to the approximate treatment employed by W. Heitler and F. London [*Z. Physik*, **44**, 455 (1927)] and developed by

thus $(a\alpha)(b\alpha)$ without specifying which electron each orbital occupies: suppose electron 1 occupies orbital a and electron 2 occupies b ; then the eigenfunction is represented by $(a\alpha)_1(b\alpha)_2$. It is equally possible, however, that the position of the electrons is reversed, so that the eigenfunction $(a\alpha)_2(b\alpha)_1$ is just as probable as the previous one. Any linear combination of eigenfunctions corresponding to the same eigenvalue is a satisfactory solution of the wave equation; two such solutions are

$$\Psi_1 = \frac{1}{\sqrt{2}} [(a\alpha)_1(b\alpha)_2 + (a\alpha)_2(b\alpha)_1], \quad (146a)$$

$$\Psi_2 = \frac{1}{\sqrt{2}} [(a\alpha)_1(b\alpha)_2 - (a\alpha)_2(b\alpha)_1], \quad (146b)$$

where the factor $1/\sqrt{2}$ is introduced so as approximately to normalize the complete eigenfunction, the orbital and spin eigenfunctions being assumed to be already normalized. In addition to the two eigenfunctions given above, six others are equally satisfactory solutions, since neither electron will have any particular preference over the other; thus,

$$\Psi_3 = \frac{1}{\sqrt{2}} [(a\alpha)_1(b\beta)_2 + (a\alpha)_2(b\beta)_1], \quad (147a)$$

$$\Psi_4 = \frac{1}{\sqrt{2}} [(a\alpha)_1(b\beta)_2 - (a\alpha)_2(b\beta)_1], \quad (147b)$$

$$\Psi_5 = \frac{1}{\sqrt{2}} [(a\beta)_1(b\alpha)_2 + (a\beta)_2(b\alpha)_1], \quad (147c)$$

$$\Psi_6 = \frac{1}{\sqrt{2}} [(a\beta)_1(b\alpha)_2 - (a\beta)_2(b\alpha)_1], \quad (147d)$$

$$\Psi_7 = \frac{1}{\sqrt{2}} [(a\beta)_1(b\beta)_2 + (a\beta)_2(b\beta)_1], \quad (147e)$$

$$\Psi_8 = \frac{1}{\sqrt{2}} [(a\beta)_1(b\beta)_2 - (a\beta)_2(b\beta)_1]. \quad (147f)$$

The Pauli Exclusion Principle.—The question now arises whether the eight eigenfunctions given above are possible, and an answer is supplied by the empirical principle first enunciated

by W. Pauli.⁹ In quantum-mechanical language, it states that *every eigenfunction for a system of two or more electrons must be antisymmetrical in every pair of electrons*;^{*} i.e., an interchange of the coordinates of any two electrons results in a reversal in sign of the eigenfunction. Applying the rule to the eigenfunctions for the two-electron system, it is seen that only Ψ_2 , Ψ_4 , Ψ_6 and Ψ_8 are possible solutions.

A special case arises when the two orbitals a and b available for the two electrons are identical; i.e., the two electrons have the same three quantum numbers n , l and m . If b is replaced by a , it is seen that Ψ_2 and Ψ_8 become zero, so that the only eigenfunctions satisfying the Pauli principle are Ψ_4 and Ψ_6 ; in both these cases the two electrons have opposite spins. This result gives the principle in its original form, thus: no two electrons in any system can have the same four quantum numbers. If n , l and m are the same, the spin quantum numbers must be $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively.

Antisymmetrical Eigenfunctions for Many-electron Systems.—

The general scheme for obtaining eigenfunctions for two-electron systems¹⁰ has been extended by J. C. Slater¹¹ to other systems. Making the assumption again that the electrons do not interact with each other and so obtaining what is called the “zero-order approximation,” a possible eigenfunction is the product of the single electron eigenfunctions. One example, for an n -electron system, is

$$\Psi = (a\alpha)_1(b\alpha)_2(c\beta)_3(d\beta)_4 \cdots (n\alpha)_n, \quad (148)$$

where a , b , c , . . . , n are the n available orbitals, α and β are the spin eigenfunctions and the subscript numerals indicate which electron occupies each particular orbital. An equally good solution can be obtained by interchanging the coordinates of any pair of electrons, e.g., 2 and 4, so that the electron 2 now occupies orbital d whereas 4 occupies b ; thus,

$$\Psi = (a\alpha)_1(b\alpha)_4(c\beta)_3(d\beta)_2 \cdots (n\alpha)_n, \quad (149)$$

⁹ W. Pauli, *Z. Physik*, **31**, 765 (1925).

^{*} The Pauli principle applies to any pair of identical elementary material particles in a system; it is not applicable to photons, as for these the eigenfunctions are symmetric.

¹⁰ W. Heitler and F. London, *ibid.*, **44**, 455 (1927).

¹¹ J. C. Slater, *Phys. Rev.*, **38**, 1109 (1931).

so that it is possible to write the general expression

$$\Psi = \mathbf{P}(a\alpha)_1(b\alpha)_2(c\beta)_3(d\beta)_4 \cdots (n\alpha)_n, \quad (150)$$

where \mathbf{P} is the permutation operator, representing the operation of interchanging the coordinates of, *i.e.*, the orbitals occupied by, any pair of electrons. The resulting eigenfunctions are, however, not antisymmetrical, as required by the Pauli principle; but the principle can be satisfied by taking a linear combination of the form

$$\Psi = \frac{1}{\sqrt{n!}} \sum \pm \mathbf{P}(a\alpha)_1(b\alpha)_2(c\beta)_3 \cdots (n\alpha)_n, \quad (151)$$

where the factor $1/\sqrt{n!}$ is introduced for approximate normalization purposes and the $[+]$ or $[-]$ sign is used before each term in the summation according as the particular permutation is obtained from the initial one by an even or odd number, respectively, of exchanges in the coordinates of pairs of electrons. Any single exchange clearly leaves the value of the eigenfunction unaltered but changes the sign, as required by the Pauli principle. This type of zero-order approximation for the many-electron system will be referred to as an "antisymmetrical eigenfunction."

The summation in (151) may be written as a determinant

$$\Psi = \begin{vmatrix} (a\alpha)_1 & (b\alpha)_1 & (c\beta)_1 & (n\alpha)_1 \\ (a\alpha)_2 & (b\alpha)_2 & (c\beta)_2 & (n\alpha)_2 \\ & & & \\ & & & \\ (a\alpha)_n & (b\alpha)_n & (c\beta)_n & (n\alpha)_n \end{vmatrix} \quad (152)$$

of which (148) is the diagonal. For convenience, this may be abbreviated in the symbolic form¹²

$$\Psi = \begin{vmatrix} a & b & c & d & \cdots & n \\ \alpha & \alpha & \beta & \beta & \cdots & \alpha \end{vmatrix}, \quad (153)$$

implying a determinant whose third and fourth columns contain β 's whereas the first, second and n th columns, among others, contain α 's. It should be noted that the eigenfunction repre-

¹² H. Eyring and G. E. Kimball, *J. Chem. Phys.*, **1**, 239 (1933).

sented by (151), (152) and (153) corresponds to the particular arrangement of spins in (148). Since every one of the n electrons may have a spin eigenfunction of α or β , it is evident there are 2^n ways of arranging the α 's and β 's among the n electrons. There will therefore be 2^n determinants, similar to that given above, each of which is a satisfactory eigenfunction for the system of n electrons.

Bond Eigenfunctions.—Since the great majority of chemical compounds, with the exception of substances containing an odd number of electrons and a few others, are nonparamagnetic and have singlet ground states, it follows that, as a general rule, the electron spins in stable molecules are coupled to give zero. It appears, therefore, that in a chemical bond the two electrons have opposite spins. The case will be considered here of systems in which all spins are coupled and the number of bonds is a maximum. Such systems are likely to be the most stable chemically. Suppose, for example, that there are four electrons, with four available orbitals a , b , c and d : in order to obtain a system with two bonds there must be two positive and two negative spins, *i.e.*, two α and two β spin eigenfunctions. Six arrangements are possible, thus,

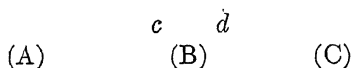
	a	b	c	d
Ψ_I	α	β	α	β
Ψ_{II}	α	α	β	β
Ψ_{III}	α	β	β	α
Ψ_{IV}	β	α	α	β
Ψ_V	β	α	β	α
Ψ_{VI}	β	β	α	α

the corresponding antisymmetrical eigenfunctions being designated $\Psi_I, \Psi_{II} \dots \Psi_{VI}$. Each of these is a satisfactory solution of the four-electron problem, as also a linear combination of them would be, and the bond eigenfunction is such a combination obtained in the following manner. Suppose it is desired to find the bond eigenfunction of $a-b$ $c-d$; *i.e.*, the electrons occupying the orbitals a and b form one bond, and those occupying c and d form another. It follows, therefore, that a and b have opposite spins and that so, also, have c and d . Of the six possible arrangements given above, only I, III, IV and V satisfy these conditions, and hence only $\Psi_I, \Psi_{III}, \Psi_{IV}$ and Ψ_V appear in

the bond eigenfunction. The appropriate sign is obtained by taking one of the antisymmetrical eigenfunctions, *e.g.*, Ψ_I , as positive, and by changing the sign for each interchange in the order of α and β ; thus Ψ_{III} is negative, Ψ_{IV} is negative, each involving one reversal, whereas Ψ_V is positive, there being two reversals. The bond eigenfunction for $a-b \text{ } c-d$, designated Ψ_A , is thus defined as

$$\Psi_A = \frac{1}{\sqrt{4}} (\Psi_I - \Psi_{III} - \Psi_{IV} + \Psi_V), \quad (154)$$

where $1/\sqrt{4}$ is the approximate normalizing factor. Four electrons can give two bonds in three ways, *viz.*,



and the bond eigenfunctions corresponding to B and C, *viz.*, $a-c \text{ } b-d$ and $a-d \text{ } b-c$, can be derived in exactly the same manner as for A, described above: they are

$$\Psi_B = \frac{1}{\sqrt{4}} (\Psi_{II} - \Psi_{III} - \Psi_{IV} + \Psi_{VI}), \quad (155)$$

and

$$\Psi_C = \frac{1}{\sqrt{4}} (\Psi_I - \Psi_{II} + \Psi_V - \Psi_{VI}). \quad (156)$$

The three bond functions are, however, not independent, for it is clear that $\Psi_C = \Psi_A - \Psi_B$; the system with crossed bonds (C) can thus be expressed in terms of those with uncrossed bonds. A rule of general applicability enunciated by G. Rumer¹³ is as follows: in any system of electrons a simple crossed bond can be described in terms of two uncrossed bonds, only the latter being independent. These independent structures, which do not involve intersecting bonds, comprise a "Rumer set" or a "canonical set"; all possible bond structures can be built up from

¹³ G. Rumer, *Göttinger Nachr.*, 377 (1932); see also H. Eyring and C. E. Sun, *J. Chem. Phys.*, 2, 299 (1934).

this independent set. In any system of n electrons the number of different structures containing the maximum number of bonds theoretically possible is

$$\frac{n!(n-s)!}{2^{\frac{1}{2}(n-s)}[\frac{1}{2}(n-s)]!};$$

but the number of independent structures forming the Rumer set is

$$\frac{(s+1)n!}{[\frac{1}{2}(n+s)+1]![\frac{1}{2}(n-s)]!};$$

where s is zero if n is an even number and unity if it is odd.

Bond Eigenfunctions and Spin.—If the electrons in any system are equally divided among positive and negative spins, it is obvious that application of the operator S_z to the eigenfunction for the system must give zero. From the chemical standpoint, it is of interest to know which arrangement of spins gives zero not only for S_z but also for the operator S^2 . It is known from quantum mechanics that this state is nonmagnetic; and since, in general, the nonmagnetic state is that of lowest energy, the state for which the operators S_z and S^2 both give zero will usually be the most stable one. Application of Eqs. (139), (140), (143) and (145) gives the required information. The operator $S_x + iS_y$ acting on α gives zero, and on β it gives $(\hbar/2\pi)\alpha$, whereas $S_x - iS_y$ gives $(\hbar/2\pi)\beta$ and zero, respectively; the result of performing these operations on a number of electrons is the sum of the values obtained by applying the operator for each electron on the complete eigenfunction (see page 55). It can be shown, as a consequence, that when $S_x + iS_y$ operates on an antisymmetrical eigenfunction of the type of (152) the result is $\hbar/2\pi$ times the sum of the determinants obtained by replacing in turn each column of α 's by zero, which gives zero, and each column of β 's by one of α 's. Similarly, the operator $S_x - iS_y$ on an antisymmetrical eigenfunction gives $\hbar/2\pi$ times the sum of all the determinants resulting from the exchange of each column of α 's in turn by one of β 's, and each column of β 's by zero.¹⁴ Two random examples may be taken for purposes of illustration: thus, employing the abbreviated form of representing the determinantal eigenfunction given on page 58,

¹⁴ Eyring and Kimball, Ref. 12.

$$\begin{aligned}
 (\mathbf{S}_x + i\mathbf{S}_y) \begin{pmatrix} a & b & c & d \\ \alpha & \beta & \alpha & \beta \end{pmatrix} &= \frac{\hbar}{2\pi} \left[\begin{pmatrix} a & b & c & d \\ 0 & \beta & \alpha & \beta \end{pmatrix} + \begin{pmatrix} a & b & c & d \\ \alpha & \beta & 0 & \beta \end{pmatrix} \right. \\
 &\quad \left. + \begin{pmatrix} a & b & c & d \\ \alpha & \alpha & \alpha & \beta \end{pmatrix} + \begin{pmatrix} a & b & c & d \\ \alpha & \beta & \alpha & \alpha \end{pmatrix} \right] \\
 &= 0.
 \end{aligned}$$

$$\begin{aligned}
 (\mathbf{S}_x - i\mathbf{S}_y) \begin{pmatrix} a & b & c & d \\ \alpha & \beta & \alpha & \alpha \end{pmatrix} &= \frac{\hbar}{2\pi} \left[\begin{pmatrix} a & b & c & d \\ \beta & \beta & \alpha & \alpha \end{pmatrix} + \begin{pmatrix} a & b & c & d \\ \alpha & \beta & \beta & \alpha \end{pmatrix} \right. \\
 &\quad \left. + \begin{pmatrix} a & b & c & d \\ \alpha & \beta & \alpha & \beta \end{pmatrix} + \begin{pmatrix} a & b & c & d \\ \alpha & 0 & \alpha & \alpha \end{pmatrix} \right] \\
 &= \frac{\hbar}{2\pi} \begin{pmatrix} a & b & c & d \\ \beta & \beta & \alpha & \alpha \end{pmatrix}.
 \end{aligned}$$

By using these rules, it is readily shown, as in the first example above, that $\mathbf{S}_x + i\mathbf{S}_y$ acting on any bond eigenfunction corresponding to the maximum number of bonds always gives zero as a result; it follows, therefore, that $(\mathbf{S}_x - i\mathbf{S}_y)(\mathbf{S}_x + i\mathbf{S}_y)$ operating on such eigenfunctions must also give zero. Since the result of applying \mathbf{S}_z to a bond eigenfunction having the maximum number of bonds is zero, it follows that the operator \mathbf{S}^2 must also yield zero* [cf. Eq. (143)]. The system corresponding to the maximum number of bonds, between unexcited atoms in their lowest states, is thus, in general, the most stable chemically.

SOLUTION OF WAVE EQUATION

The Variation Method.—It is only for the one-electron system, as in the hydrogen atom, for example, that a complete solution of the Schrödinger equation can be given; but for systems of two or more electrons, such as are of interest for present purposes, exact solution is not feasible. It is the practice, therefore, to employ approximation methods; one of these, which will be discussed here, is the "variation" treatment, and the other, for which reference should be made to any of the standard textbooks on quantum mechanics,¹⁵ is based on "perturbation theory."

* If the system contains an odd number of electrons, then the operation of \mathbf{S}_z and \mathbf{S}^2 on the maximum bond eigenfunction gives $\frac{1}{2}(\hbar/2\pi)$ and $\frac{3}{4}(\hbar/2\pi)^2$, respectively; these are the lowest possible values.

¹⁵ See, for example, L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics," Chap. VI, McGraw-Hill Book Company, Inc., 1935;

Any function ψ can be expanded in terms of the normalized, orthogonal eigenfunctions ϕ_i of any operator (see page 44), *e.g.*, the operator for energy \mathbf{H} ; thus,

$$\psi = \sum_i a_i \phi_i, \quad (157)$$

where

$$a_i = \int \bar{\phi}_i \psi \, d\tau. \quad (158)$$

Suppose ψ is normalized, as is always possible; then,

$$\int \bar{\psi} \psi \, d\tau = \sum_i \bar{a}_i a_i \int \bar{\phi}_i \phi_i \, d\tau = 1; \quad (159)$$

$$\therefore \sum_i \bar{a}_i a_i = 1. \quad (160)$$

According to the Schrödinger equation, $\mathbf{H}\phi_i = E_i\phi_i$, and so

$$\int \bar{\phi}_i \mathbf{H} \phi_i \, d\tau = E_i \int \bar{\phi}_i \phi_i \, d\tau = E_i. \quad (161)$$

If the integral I is defined by

$$I = \int \bar{\psi} \mathbf{H} \psi \, d\tau, \quad (162)$$

it follows from Eqs. (157) and (161) that

$$I = \sum_i \bar{a}_i a_i E_i. \quad (163)$$

If the lowest eigenvalue of \mathbf{H} for the eigenfunctions ϕ_i is E_1 , then it can be seen that I has the lowest value (E_1) when $\bar{a}_1 a_1 = 1$ and $\bar{a}_i a_i = 0$ for $i \neq 1$. It may be concluded, therefore, that, by choosing ψ , the so-called "variation function," at random, it is never possible to find a function which yields a value for I less than the energy E_1 , *i.e.*, the lowest eigenvalue for the operator \mathbf{H} . Further, the ψ that gives the lowest value of E_1 is the corresponding eigenfunction ϕ_1 .

If there is more than one state with the energy E_1 , *i.e.*, if the level is degenerate, then a second eigenfunction can be found by

using the normalized eigenfunction ψ'_2 , viz., $\psi_2 - \left(\int \psi_2 \psi_1 d\tau\right) \psi_1$ (see page 47), which is orthogonal to ψ_1 , and seeking the lowest energy by varying ψ_2 as before. If the lowest state is not degenerate, then this variation will lead to the second lowest level. In this way all the levels can be found, in principle, by repeating the variation process; the new function which is being varied at each stage must always be taken as orthogonal to those obtained previously.

A useful application of the variation principle derived above is to the case in which the variation function ψ can be expressed in terms of the sum of any arbitrary set of linearly independent functions χ : thus,

$$\psi = \sum_i c_i \chi_i. \quad (164)$$

The χ 's need not be eigenfunctions for \mathbf{H} or, necessarily, orthogonal, although there would be no loss of generality in assuming both the χ 's and ψ to be normalized. Consider the integral J , defined by

$$J = \int \psi(\mathbf{H} - E)\psi d\tau; \quad (165)$$

if ψ and E are the corresponding eigenfunction and eigenvalue for \mathbf{H} , then, by the Schrödinger equation, J will be zero. If the χ 's in Eq. (164) were a complete set of functions, variation of the c 's so as to make J equal to zero would then give the required values of ψ and E . Even if the set of χ 's is incomplete, it is still possible to obtain a best value of E by means of the variation principle. It has been seen above that the lowest value of the integral I , defined by Eq. (162), approximates most closely to E_1 , the lowest eigenvalue for \mathbf{H} . Hence, it follows from (165) that, even if J is not zero, it should at least be a minimum; i.e.,

$$\delta J = \frac{\partial J}{\partial c_1} \delta c_1 + \frac{\partial J}{\partial c_2} \delta c_2 + \frac{\partial J}{\partial c_3} \delta c_3 + \cdots + \frac{\partial J}{\partial c_n} \delta c_n = 0. \quad (166)$$

If $\delta c_1, \delta c_2, \dots, \delta c_n$ are independent parameters, not equal to zero, then J will be zero only if

$$\frac{\partial J}{\partial c_1} = \frac{\partial J}{\partial c_2} = \cdots = \frac{\partial J}{\partial c_n} = 0. \quad (167)$$

Substituting in Eq. (165) the values of ψ and $\bar{\psi}$ given by the

expansion in (164),

$$J = \int \sum_i \bar{c}_i \bar{\chi}_i (\mathbf{H} - E) \sum_i c_i \chi_i d\tau; \quad (168)$$

and since $\partial J / \partial c_1 = 0$, it follows that

$$c_1 \left(\int \bar{\chi}_1 \mathbf{H} \chi_1 d\tau - E \int \bar{\chi}_1 \chi_1 d\tau \right) + c_2 \left(\int \bar{\chi}_1 \mathbf{H} \chi_2 d\tau - E \int \bar{\chi}_1 \chi_2 d\tau \right) \\ + \cdots + c_n \left(\int \bar{\chi}_1 \mathbf{H} \chi_n d\tau - E \int \bar{\chi}_1 \chi_n d\tau \right) = 0. \quad (169)$$

Similar equations will result for $\partial J / \partial c_2 = 0$, etc.; and consequently there will be a set of n linear equations which may be written

$$c_1(H_{11} - \Delta_{11}E) + c_2(H_{12} - \Delta_{12}E) + \cdots + c_n(H_{1n} - \Delta_{1n}E) = 0 \\ c_1(H_{21} - \Delta_{21}E) + c_2(H_{22} - \Delta_{22}E) + \cdots + c_n(H_{2n} - \Delta_{2n}E) = 0$$

$$c_1(H_{n1} - \Delta_{n1}E) + c_2(H_{n2} - \Delta_{n2}E) + \cdots + c_n(H_{nn} - \Delta_{nn}E) = 0, \quad (170)$$

where the following abbreviations (*cf.* page 48) are employed:

$$H_{ij} = \int \bar{\chi}_i \mathbf{H} \chi_j d\tau \quad \text{and} \quad \Delta_{ij} = \int \bar{\chi}_i \chi_j d\tau. \quad (171)$$

Solving the set of Eqs. (170) for c_1 , the result is

$$c_1 = \frac{\begin{vmatrix} 0 & (H_{12} - \Delta_{12}E) & (H_{13} - \Delta_{13}E) & \cdots & (H_{1n} - \Delta_{1n}E) \\ 0 & (H_{22} - \Delta_{22}E) & (H_{23} - \Delta_{23}E) & \cdots & (H_{2n} - \Delta_{2n}E) \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & (H_{n2} - \Delta_{n2}E) & (H_{n3} - \Delta_{n3}E) & \cdots & (H_{nn} - \Delta_{nn}E) \end{vmatrix}}{\begin{vmatrix} (H_{11} - \Delta_{11}E) & (H_{12} - \Delta_{12}E) & \cdots & (H_{1n} - \Delta_{1n}E) \\ (H_{21} - \Delta_{21}E) & (H_{22} - \Delta_{22}E) & \cdots & (H_{2n} - \Delta_{2n}E) \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ (H_{n1} - \Delta_{n1}E) & (H_{n2} - \Delta_{n2}E) & \cdots & (H_{nn} - \Delta_{nn}E) \end{vmatrix}} \quad (172)$$

Since the numerator is zero, c_1 can have a nontrivial value, *i.e.*, one different from zero, only if the determinant in the denom-

inator is zero; thus

$$\begin{aligned} & (H_{11} - \Delta_{11}E) (H_{12} - \Delta_{12}E) (H_{13} - \Delta_{13}E) \cdots (H_{1n} - \Delta_{1n}E) \\ & (H_{21} - \Delta_{21}E) (H_{22} - \Delta_{22}E) (H_{23} - \Delta_{23}E) \cdots (H_{2n} - \Delta_{2n}E) \end{aligned}$$

$$\begin{aligned} & (H_{n1} - \Delta_{n1}E) (H_{n2} - \Delta_{n2}E) (H_{n3} - \Delta_{n3}E) \cdots (H_{nn} - \Delta_{nn}E) \\ & = 0. \quad (173) \end{aligned}$$

Every H and Δ in this determinant, frequently referred to as the "secular equation" for the problem, has a definite numerical value, and so it is an equation of the n th degree in E and has n roots, *viz.*, $E_1, E_2, \dots, E_k, \dots, E_n$.

In order to find the eigenfunctions corresponding to the E values, the root E_k may be substituted for E in the set of Eqs. (170); and if $n - 1$ of the resulting equations are each divided by c_n , it is possible to solve explicitly for the $n - 1$ ratios c_1/c_n to c_{n-1}/c_n . This set of ratios, together with the normalizing condition for ψ , *viz.*,

$$\int \psi \psi \, d\tau = \sum c_i c_j \Delta_{ij} = 1, \quad (174)$$

leads to a solution for all the c 's, and so the eigenfunction ψ_k which goes with the energy value E_k can be determined from Eq. (164). In this way, there is obtained the best possible set of approximate eigenfunctions and eigenvalues that can be made from a linear combination of n functions designated by χ_i . The same set of ψ 's and E 's can be arrived at by the perturbation method.

APPLICATION OF THE APPROXIMATION METHODS

The potential energy V for a system of n electrons and n fixed nuclei is given by

$$V = - \sum_{Ai} \frac{z_A e^2}{r_{Ai}} + \sum_{AB} \frac{z_A z_B e^2}{r_{AB}} + \sum_{ij} \frac{e^2}{r_{ij}}, \quad (175)$$

where e is the electronic (unit) charge, r_{Ai} is the distance of the i th electron from the nucleus A , r_{AB} is the distance between any pair of nuclei A and B carrying charges z_A and z_B , respectively,

and r_{ij} is the distance between any pair of electrons i and j (cf. Fig. 2). The Hamiltonian operator for the system is, therefore,

$$\mathbf{H} = -\frac{\hbar^2}{8\pi^2m} \sum_i \nabla_i^2 - \sum_{A,i} \frac{z_A \mathcal{E}^2}{r_{Ai}} + \sum_{A,B} \frac{z_A z_B \mathcal{E}^2}{r_{AB}} + \sum_{i,j} \frac{\mathcal{E}^2}{r_{ij}}, \quad (176)$$

the relative kinetic energy of the nuclei having been neglected, because of their large mass, as compared with that of the electrons. The term $\sum_{i,j} \frac{\mathcal{E}^2}{r_{ij}}$ represents the interaction between

pairs of electrons; and if this is omitted, the Hamiltonian, apart from the constant terms for the fixed nuclei, can be divided up into n separate operators, one for each electron. The omission of $\sum_{i,j} \frac{\mathcal{E}^2}{r_{ij}}$ may thus be assumed to give the Hamiltonian oper-

ator for the unperturbed state in which there is no interaction between electrons. It has been seen (page 58) that under the latter conditions the antisymmetric eigenfunction should be a reasonably satisfactory solution, and so this may be taken as applying to the unperturbed state. As a result of electron spin, however, there are 2^n possible eigenfunctions (page 59) corresponding to a given eigenvalue;

i.e., the system of n electrons shows a 2^n -fold spin degeneracy.

The Four-electron Problem.¹⁶—It is apparent that, in general, the n -electron system can be treated as a variation problem involving degeneracy, and its solution would evidently require the setting up of a secular equation, analogous to (173), with 2^n roots. Even for as few as four electrons the secular equation would have 2^4 , *i.e.*, 16, roots, and a complete solution would, at first sight, appear very difficult. In practice, however, the 16-rowed determinant, for the four-electron problem, can be split up into a number of simpler determinants, because the quantities H_{ab} and Δ_{ab} , as defined by Eq. (171), are zero unless the

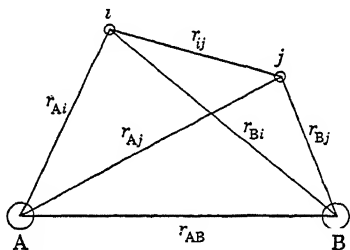
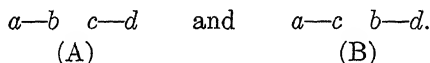


FIG. 2.—System of two nuclei (A and B) and two electrons (i and j).

¹⁶ Slater, Ref. 11.

sum of the spins is the same in ψ_a and ψ_b (see page 70). Each of the lower order determinants making up the secular equation, therefore, involves levels with the same resultant spin. For example the 16-rowed determinant for the four-electron problem splits up into the product of five simpler determinants corresponding to states in which the total spin values are $+2$, $+1$, 0 , -1 and -2 , respectively. By the use of certain devices the secular equation can often be solved in the simpler cases without serious difficulty, but it is not necessary to discuss them here.

From the chemical standpoint the most important state is the most stable one, *viz.*, the one for which the operation of S^2 and S_z on the bond eigenfunction gives zero. It was shown above that this is the one with the maximum number of bonds, and hence for the four-electron system it is necessary to consider only the two independent structures



It is evident, therefore, that the four-electron problem has now been reduced to such an extent that the secular equation of particular interest consists of a determinant of the second order; thus,

$$\begin{vmatrix} H_{AA} - \Delta_{AA}E & H_{AB} - \Delta_{AB}E \\ H_{BA} - \Delta_{BA}E & H_{BB} - \Delta_{BB}E \end{vmatrix} = 0, \quad (177)$$

where

$$H_{AA} = \int \Psi_A \mathbf{H} \Psi_A d\tau$$

and

$$\Delta_{AA} = \int \Psi_A \Psi_A d\tau, \text{ etc.}^*$$

It should be noted that since the Hamiltonian is Hermitian and ψ_A and ψ_B are real, $H_{AB} = H_{BA}$ (see page 35); hence, it follows that

$$(H_{AA} - \Delta_{AA}E)(H_{BB} - \Delta_{BB}E) - (H_{AB} - \Delta_{AB}E)^2 = 0, \quad (178)$$

so that if H_{AA} , etc., and the corresponding Δ 's are known, it should be possible to solve the quadratic for E . The values of

* The eigenfunctions employed are real, so that $\bar{\psi}$ may be replaced by ψ .

Ψ_A and Ψ_B are known in terms of the antisymmetric eigenfunctions $\Psi_I, \Psi_{II}, \dots, \Psi_{VI}$ (pages 59 to 60), and hence it is possible to write the integrals of the type $\int \Psi_A \Psi_A d\tau$ and $\int \Psi_A \mathbf{H} \Psi_A d\tau$ in terms of those of the form $\int \Psi_I \Psi_I d\tau$, $\int \Psi_I \Psi_{II} d\tau$, $\int \Psi_I \mathbf{H} \Psi_I d\tau$, $\int \Psi_I \mathbf{H} \Psi_{II} d\tau$, etc. Since each $\Psi_I, \Psi_{II}, \dots, \Psi_{VI}$ involves a determinant, the result would, at first sight, appear to be very cumbersome; in practice, however, considerable simplification results as a consequence of the inclusion of the spin eigenfunctions.

The integral $H_{I,II}$, i.e., the matrix component of the operator \mathbf{H} between the eigenfunctions Ψ_I and Ψ_{II} , for example, is given by

$$H_{I,II} = \int \Psi_I \mathbf{H} \Psi_{II} d\tau, \quad (179)$$

and the antisymmetric (determinantal) eigenfunctions Ψ_I and Ψ_{II} on page 59 are

$$\Psi_I = \frac{1}{\sqrt{4!}} \sum \pm \mathbf{P}_I (a\alpha)_1 (b\beta)_2 (c\alpha)_3 (d\beta)_4, \quad (180)$$

$$\Psi_{II} = \frac{1}{\sqrt{4!}} \sum \pm \mathbf{P}_{II} (a\alpha)_1 (b\alpha)_2 (c\beta)_3 (d\beta)_4. \quad (181)$$

$$H_{I,II} = \frac{1}{4!} \int \left[\sum \pm \mathbf{P}_I (a\alpha)_1 (b\beta)_2 (c\alpha)_3 (d\beta)_4 \right] \mathbf{H} \left[\sum \pm \mathbf{P}_{II} (a\alpha)_1 (b\alpha)_2 (c\beta)_3 (d\beta)_4 \right] d\tau, \quad (182)$$

where \mathbf{P}_I and \mathbf{P}_{II} denote the permutation operators. Since these permutations include every possible exchange of the coordinates of pairs of electrons, as explained previously (page 58), the result will be unchanged if the operators $\sum \pm \mathbf{P}_I$ and $\sum \pm \mathbf{P}_{II}$ are multiplied by another permutation operator \mathbf{P} . If the latter is chosen successively to reverse each \mathbf{P}_I in the summation, i.e., $\mathbf{P} = \mathbf{P}_I^{-1}$, and $\mathbf{P}_I^{-1} \mathbf{P}_I$ is the identity operator that leaves the original arrangement unchanged, then every term in the first (left-hand) summation will be the same; it is thus possible to write

$$\sum \mathbf{P}_I^{-1} \mathbf{P}_I (a\alpha)_1 (b\beta)_2 (c\alpha)_3 (d\beta)_4 = 4! [(a\alpha)_1 (b\beta)_2 (c\alpha)_3 (d\beta)_4], \quad (183)$$

since there are $4!$ terms in the summation. It follows, therefore,

that

$$H_{I,II} = \int [(a\alpha)_1(b\beta)_2(c\alpha)_3(d\beta)_4] \mathbf{H}[\Sigma \pm \mathbf{P}'(a\alpha)_1(b\alpha)_2(c\beta)_3(d\beta)_4], \quad (184)$$

where the permutation operator \mathbf{P}' replaces $\mathbf{P}_I^{-1}\mathbf{P}_{II}$.^{*} The integral $H_{I,II}$ has now been reduced to $4!$ instead of $(4!)^2$ terms, and a still further reduction is possible by making the assumption already used (page 55) that the orbital and spin parts of the electron eigenfunctions do not interact. One of the 24 terms of (184), to which the symbol I may be given, is

$$I = \int [(a\alpha)_1(b\beta)_2(c\alpha)_3(d\beta)_4] \mathbf{H}[(a\alpha)_2(b\alpha)_3(c\beta)_1(d\beta)_4] d\tau, \quad (185)$$

in which there have been two changes of electron coordinates, *viz.*, 1 and 2, and 2 and 3, so that the expression has a positive sign. If the Hamiltonian does not operate on the spin eigenfunctions, then the two parts may be separated thus:

$$I = \int (a_1b_2c_3d_4) \mathbf{H}(a_2b_3c_1d_4) d\tau \int \alpha_1\beta_1 d\omega \int \alpha_2\beta_2 d\omega \int \alpha_3^2 d\omega \int \beta_4^2 d\omega, \quad (186)$$

where $d\omega$ is an element of spin space. The spin eigenfunctions for the separate electrons are always assumed to be normalized and mutually orthogonal (page 44), so that

$$\int \alpha_1\beta_1 d\omega = 0; \quad \int \alpha_2\beta_2 d\omega = 0; \quad \int \alpha_3^2 d\omega = 1; \quad \int \beta_4^2 d\omega = 1; \quad (187)$$

from which it follows at once that I must be zero. It can be readily seen that other analogous terms will be zero unless the spins in the eigenfunctions before and after the Hamiltonian match exactly; in the latter circumstances the spin portion of the integral is unity.[†] The matrix components of the operator \mathbf{H} (such as $H_{I,I}$, $H_{I,II}$, etc.) that are not zero will therefore contain orbital functions only. In the case under consideration

^{*} It will be observed that the factor $1/4!$ in Eq. (182), arising from the normalization factors in the antisymmetric eigenfunctions, cancels out with $4!$ in Eq. (183); this is not a matter of chance, for the approximate normalization factor was chosen partly with this end in view.

[†] It will be evident that the *total* z -component of the spins must be the same in the two eigenfunctions; otherwise, all the terms will be zero.

the terms of $H_{I,II}$ that are not zero are

$$\begin{aligned}
 & - \int [(a\alpha)_1(b\beta)_2(c\alpha)_3(d\beta)_4] \mathbf{H}[(a\alpha)_1(b\alpha)_3(c\beta)_2(d\beta)_4] d\tau \quad bc \\
 & + \int [(a\alpha)_1(b\beta)_2(c\alpha)_3(d\beta)_4] \mathbf{H}[(a\alpha)_3(b\alpha)_1(c\beta)_2(d\beta)_4] d\tau \quad ab \text{ and } ac \\
 & + \int [(a\alpha)_1(b\beta)_2(c\alpha)_3(d\beta)_4] \mathbf{H}[(a\alpha)_1(b\alpha)_3(c\beta)_4(d\beta)_2] d\tau \quad cd \text{ and } bd \\
 & - \int [(a\alpha)_1(b\beta)_2(c\alpha)_3(d\beta)_4] \mathbf{H}[(a\alpha)_3(b\alpha)_1(c\beta)_4(d\beta)_2] d\tau \quad ab, cd \text{ and } ad.
 \end{aligned}$$

The permutations of the coordinates are indicated in the last column; thus, "ab and ac" means that the coordinates of a and b are first interchanged and then those of a and c , so that the original arrangement of orbitals $a_1b_2c_3d_4$, sometimes written $(abcd)$, becomes first $a_2b_1c_3d_4$, i.e., $(bacd)$, and then $a_3b_1c_2d_4$, i.e., $(bcad)$. The first and fourth of these integrals have negative signs, since they result from an odd number of exchanges, whereas the others, involving two interchanges of coordinates, have positive signs. If the orbital functions were mutually orthogonal, the integrals resulting from the exchange of more than one pair of electrons would be zero. In practice, the eigenfunctions are not exactly orthogonal; but since the departure from orthogonality is not considerable, the so-called "multiple-exchange integrals" are regarded as so small as to be negligible.¹⁷ It follows, therefore, that only the first of the four integrals given above, which is a "single-exchange integral," need be considered; hence,

$$H_{I,II} = - \int (a_1b_2c_3d_4) \mathbf{H}(a_1b_3c_2d_4) d\tau, \quad (188)$$

the spin contribution being unity. If the numerals are left out and the orbitals are written in the order of the subscripts, Eq. (188) becomes

$$H_{I,II} = - \int (abcd) \mathbf{H}(acbd) d\tau, \quad (189)$$

and this has been still further abbreviated to

$$H_{I,II} = -(abcd) |\mathbf{H}|(acbd), \quad (190)$$

or merely to $-(bc)$, which implies a single-exchange integral involving an interchange in the coordinates of b and c .

It is apparent that by a series of operations the $(4!)^2$ terms which might be thought to contribute to the matrix component

¹⁷ Slater, Ref. 11.

$H_{I,II}$ have been reduced to one, and the same treatment can be applied in other cases. The results can, fortunately, be generalized in the following simple statement: The matrix element between two *different* antisymmetric eigenfunctions is zero unless the two eigenfunctions differ only by a single interchange of spins on two orbitals, in which case it is the negative of the exchange integral between these orbitals. In the case of $H_{I,II}$ the two eigenfunctions may be written (cf. page 58)

$$\begin{array}{cc} \text{I} & \text{II} \\ \begin{pmatrix} a & b & c & d \\ \alpha & \beta & \alpha & \beta \end{pmatrix} & \begin{pmatrix} a & b & c & d \\ \alpha & \alpha & \beta & \beta \end{pmatrix} \end{array}$$

the only difference being an interchange of spins on b and c , so that the matrix component is $-(bc)$, as found above. By means of this rule, it is possible to write down directly all the non-diagonal components of the matrix.

It is now necessary to consider the diagonal matrix element, *i.e.*, between any antisymmetric (determinantal) eigenfunction and itself, *e.g.*, $H_{I,I}$. Working in the same manner as described above, we find that

$$H_{I,I} = \int (abcd)\mathbf{H}(abcd) d\tau - \int (abcd)\mathbf{H}(cbad) d\tau - \int (abcd)\mathbf{H}(adcb) d\tau, \quad (191)$$

which may be written

$$H_{I,I} = (abcd)|H|(abcd) - (abcd)|H|(cbad) - (abcd)|H|(adcb). \quad (192)$$

The first integral, which is the matrix component of \mathbf{H} between two identical orbital eigenfunctions, is known as the "coulomb integral," represented by the symbol Q . It is given this name because it is the result of the coulomb interaction as it would be given in classical theory between every pair of electrons in the system under discussion, taking into account the cloud distribution of electrons required by wave mechanics (see page 31). The matrix element $H_{I,I}$ is thus

$$H_{I,I} = Q - (ac) - (bd) \quad (193)$$

where (ac) and (bd) represent the single-exchange, or resonance, integrals.

The general rule for finding a diagonal component of the matrix formed from antisymmetric eigenfunctions is to take the coulomb integral and subtract all exchange integrals between orbitals having the same spin. In the element $H_{I,I}$, the orbitals a and c are associated with the spin function α , and b and d with β , so that Eq. (193) follows directly from the rule.

Since, as shown on page 60,

$$\Psi_A = \frac{1}{\sqrt{4}} (\Psi_I - \Psi_{III} - \Psi_{IV} + \Psi_V),$$

$$H_{AA} = \frac{1}{4}(H_{I,I} + H_{III,III} + H_{IV,IV} + H_{V,V} - 2H_{I,III} - 2H_{I,IV} + 2H_{I,V} + 2H_{III,IV} - 2H_{III,V} - 2H_{IV,V}).^* \quad (194)$$

The double exchange elements $H_{I,V}$ and $H_{III,IV}$ are zero, and the others obtained by the rule given above are

$$\begin{aligned} H_{I,I} &= Q - (ac) - (bd) & H_{I,III} &= -(cd) \\ H_{III,III} &= Q - (ad) - (bc) & H_{I,IV} &= -(ab) \\ H_{IV,IV} &= Q - (bc) - (ad) & H_{III,V} &= -(ab) \\ H_{V,V} &= Q - (ac) - (bd) & H_{IV,V} &= -(cd). \end{aligned} \quad (195)$$

Hence, by Eq. (194),

$$H_{AA} = \frac{1}{4}(4Q - 2ac - 2bd - 2ad - 2bc + 4ab + 4cd) \quad (196)$$

$$= Q - \frac{1}{2}(ac + bd + ad + bc) + (ab + cd). \quad (197)$$

Although the evaluation of H_{AA} , etc., in terms of the coulomb and exchange (resonance) integrals is relatively simple, the procedure must evidently become complicated when more than four electrons are involved. However, by the use of certain general rules, which are a direct consequence of the method of treatment given, the labor is greatly diminished.¹⁸ In order to find the matrix component of \mathbf{H} between any two bond eigenfunctions, the two bond systems are first written down; thus, for the component H_{AA} , the bond systems (A and A) are both $a-b \ c-d$. If a start is made by assigning a spin of α arbitrarily to the a 's, then the spin of the b 's must be β , viz.,

$$\begin{array}{cc} a-b & c-d \\ \alpha \ \beta & \alpha \ \beta \end{array}$$

Thus, giving a definite spin to a fixes that of b only, and not of

* Since \mathbf{H} is Hermitian, $H_{I,III} = H_{III,I}$, etc.

¹⁸ Cf. H. Eyring and G. E. Kimball, *J. Chem. Phys.*, **1**, 626 (1933).

any other electron, so that a and b are said to form a cycle, designated by the symbol (a/b) . For later convenience the numerator contains the orbital associated with spin α and the denominator that associated with β . It is now necessary to assign arbitrarily a spin to c , *e.g.*, α ; then d must have spin β , thus:

$$\begin{array}{cc} a-b & c-d \\ \alpha & \beta \end{array} \quad \begin{array}{cc} a-b & c-d \\ \alpha & \beta \end{array}$$

Hence, c and d also form a cycle (c/d). The cycle system for the matrix component H_{AA} is thus $(a/b)(c/d)$.* The matrix component itself is then found by the following general expression: if x is the number of cycles and y the number of bonds, then

$$H_{LM} = \frac{2^x}{2^y} \{ Q + \frac{1}{2} [\sum (\text{single-exchange integrals between electrons in the same cycle with opposite spins}) - \sum (\text{single-exchange integrals between electrons in the same cycle with the same spin}) - \frac{1}{2} \sum (\text{all single-exchange integrals})] \}.$$

In the case of H_{AA} , it follows, therefore, that

$$H_{AA} = \frac{2^2}{2^2} \{ Q + \frac{1}{2} [(ab + cd) - 0] - \frac{1}{2} [(ab) + (cd) + (ac) + (bd) + (ad) + (bc)] \} \quad (198)$$

$$= Q - \frac{1}{2}(ac + bd + ad + bc) + (ab + cd), \quad (199)$$

as found by the detailed method described above [*cf.* Eq. (197)]. By the use of the generalization, it is readily shown that

$$H_{BB} = Q - \frac{1}{2}(ab + cd + ad + bc) + (ac + bd). \quad (200)$$

To determine H_{AB} the two bond systems A and B are written down; and, upon assigning to a the arbitrary spin α , b must have the spin β as shown above.

$$\begin{array}{cc} \text{(A)} & \text{(B)} \\ a-b & a-c \\ \alpha & \beta \end{array} \quad \begin{array}{cc} c-d & b-d \\ \alpha & \beta \end{array}$$

It is now necessary that c should have the spin β and d should have

* This is really a procedure for finding the number of determinantal eigenfunctions that the two bond functions have in common; since the spin of a could have been initially chosen arbitrarily in two ways, it can be readily seen that this number is 2^x , where x is the number of cycles.

spin α ; thus,

$$\begin{array}{cc} a-b & c-d \\ \alpha \quad \beta & \beta \quad \alpha \end{array} \qquad \begin{array}{cc} a-c & b-d \\ \alpha \quad \beta & \beta \quad \alpha \end{array}$$

There is here only one cycle, which may be written (ad/bc) ; hence, it follows that

$$H_{AB} = \frac{2}{2^2} \{Q + \frac{3}{2}[(ab + ac + bd + cd) - (ad + bc)] - \frac{1}{2}[(ab) + (ac) + (bd) + (cd) + (ad) + (bc)]\} \quad (201)$$

$$= \frac{1}{2}[Q + (ab) + (ac) + (bd) + (cd) - 2(ad) - 2(bc)]. \quad (202)$$

The solution of Eq. (178) now requires only a knowledge of the Δ 's. Take, for example, Δ_{AA} , *i.e.*,

$$\Delta_{AA} = \int \Psi_A \Psi_A d\tau;$$

since Ψ_A can be expressed in terms of Ψ_I , Ψ_{III} , Ψ_{IV} and Ψ_V , it is seen that Δ_{AA} is given by an expression exactly analogous to that for H_{AA} in Eq. (194), except that the operator is unity; *i.e.*, the symbol Δ replaces each H in the expression, where $\Delta_{I,I} = \int \Psi_I \Psi_I d\tau$, etc. If the approximation is made of taking the antisymmetric eigenfunctions to be normalized and mutually orthogonal, terms such as $\Delta_{I,I}$ between two identical eigenfunctions are equal to unity, whereas those between different eigenfunctions will be zero; thus,

$$\Delta_{AA} = \frac{1}{4}(1 + 1 + 1 + 1) = 1. \quad (203)$$

It is easily seen that in general the value of Δ is equal to the coefficient of Q in the matrix of \mathbf{H} , so that $\Delta_{BB} = 1$ and $\Delta_{AB} = \frac{1}{2}$. Insertion of these results in Eq. (178) gives

$$\begin{aligned} \{Q - \frac{1}{2}[(ac) + (bd) + (ad) + (bc)] + (ab) + (cd) - E\} \\ \{Q - \frac{1}{2}[(ab) + (cd) + (ad) + (bc)] + (ac) + (bd) - E\} \\ - \frac{1}{4}[Q + (ab) + (ac) + (bd) + (cd) \\ - 2(ad) - 2(bc) - E]^2 = 0. \end{aligned} \quad (204)$$

If the exchange integrals (ab) and (cd) are replaced by α_1 and α_2 ,* (ac) and (bd) by β_1 and β_2 , and (bc) and (ad) by γ_1 and γ_2 , the

* α and β as used here and subsequently should not be confused with the same symbols previously employed to represent spins.

solutions of the quadratic are

$$E = Q \pm \left\{ \frac{1}{2}[(\alpha_1 + \alpha_2) - (\beta_1 + \beta_2)]^2 + \frac{1}{2}[(\beta_1 + \beta_2) - (\gamma_1 + \gamma_2)]^2 + \frac{1}{2}[(\gamma_1 + \gamma_2) - (\alpha_1 + \alpha_2)]^2 \right\}^{1/2}. \quad (205)$$

Of these two solutions the one with the negative sign preceding the square root represents the state of lowest energy with respect to the separated electrons and so corresponds to the stable system; hence, Eq. (205) may be written in the form, generally referred to as the London equation,¹⁹

$$E = Q - \left\{ \frac{1}{2}[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2] \right\}^{1/2}, \quad (206)$$

where α is substituted for $\alpha_1 + \alpha_2$, β for $\beta_1 + \beta_2$ and γ for $\gamma_1 + \gamma_2$.

Coulombic and Exchange (Resonance) Energies.—The significance of the quantities involved in Eqs. (205) and (206) may be seen from another angle in the following manner. Suppose two of the electrons, *e.g.*, *c* and *d*, were moved to an infinite distance from each other and from *a* and *b*. Then the energy of the electron pair *ab* would contain in place of *Q* in (205) a coulombic term *A* for the attraction between *a* and *b*, and all the exchange integrals other than α_1 , which is equivalent to (*ab*), would drop out; hence, Eq. (205) reduces to

$$E_{ab} = A_1 + \alpha_1. \quad (207)$$

A similar equation $E_{cd} = A_2 + \alpha_2$ can be obtained for the energy of the electrons *c* and *d*, with *a* and *b* at infinity; and analogous results are derived in a similar manner for the other four possible pairs of electrons, as shown in Fig. 3. The quantities $A_1, A_2, B_1, B_2, C_1, C_2$ are the coulombic energies for the various electron pairs; and when the four electrons are brought together, so that the six electrostatic attractions are operative, the total coulombic energy is equal to *Q* in Eq. (205), thus:

$$Q = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 \quad (208)$$

The total coulombic energy *Q* is seen to be the sum of the coulombic energies of all the separate pairs of electrons in the system.

The energy of the system involving the pair of electrons *ab*, when the other pair is at a large distance, is $A_1 + \alpha_1$; of this, A_1 is the coulombic energy and hence α_1 is the exchange energy, or resonance energy, of this pair. In the same way, it is evident

¹⁹ F. London, "Probleme der modernen Physik (Sommerfeld Festschrift)," p. 104, 1928; *Z. Elektrochem.*, **35**, 552 (1929).

that α_2 , β_1 , β_2 , γ_1 and γ_2 may be regarded as the exchange, or resonance, energy contributions to the energy of the electron pairs cd , ac , bd , bc and ad , respectively, when the other pair is removed.

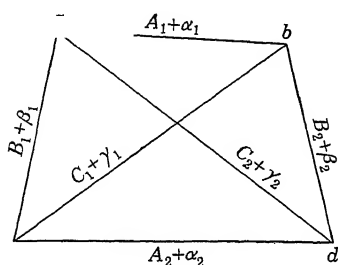


FIG. 3.—Coulombic and exchange energies for system of four electrons.

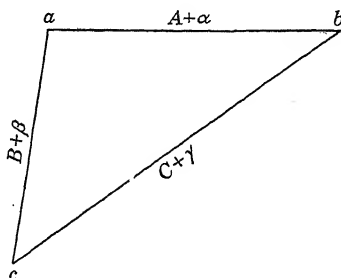


FIG. 4.—Coulombic and exchange energies for system of three electrons.

The Three-electron Problem.—The equation for the energy of a system of three electrons may be readily derived from that for a four-electron system, by imagining one of the electrons, *e.g.*, d , removed. The arrangement in Fig. 3 then becomes as shown in Fig. 4. The quantities A_2 , B_2 , C_2 and α_2 , β_2 and γ_2 disappear; and, upon writing A , B and C without subscripts for A_1 , B_1 and C_1 , and α , β and γ for α_1 , β_1 and γ_1 , it is seen that Eq. (205) becomes

$$E = Q - \{\frac{1}{2}[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2]\}^{1/2}, \quad (209)$$

which is identical in form with Eq. (206) except that the quantities α , β and γ now each refer to one electron pair only, whereas in Eq. (206) they were the sum of the exchange energies for two pairs. The coulombic energy Q is now equal to $A + B + C$, since there are only three possible pairs to consider.

Systems of More than Four Electrons.—Although the equations for the energies of three- and four-electron systems will be mostly used in this book, it is sometimes desirable to deal with the problem of five, six or more electrons.²⁰ The method employed is, in principle, identical with the general procedure already described (pages 66ff.) A system involving an odd number of electrons is treated as one with the next higher even

²⁰ A. Sherman and H. Eyring, *J. Am. Chem. Soc.*, **54**, 2661 (1932); G. E. Kimball and H. Eyring, *ibid.*, **54**, 3876 (1932); A. Sherman, C. E. Sun and H. Eyring, *J. Chem. Phys.*, **3**, 49 (1935); Eyring and Kimball, Ref. 12.

number, and then the additional electron is assumed to be moved to infinity, so that all terms containing reference to it are ignored. The method is thus equivalent to that employed above to derive the energy of the three-electron system. The number of terms in the secular equation for the energy increases rapidly as the number of electrons is increased; thus, for a six-electron system the determinant that has to be solved is of the fifth order, whereas for the eight-electron problem it is of the fourteenth order. The stable state of the system is that corresponding to the solution giving the largest negative value of the energy with reference to the separated electrons.

Since the Hamiltonian operator for any number of electrons can be written down without difficulty (page 67), it should be possible, in principle, to derive all the matrix components of \mathbf{H} and of unity required for the solution of any secular equation, provided that the bond eigenfunctions are known. It is obvious, however, that with increasing numbers of electrons and increasing complexity of both the Hamiltonian operator and the eigenfunctions the required integration would become a stupendous task; in fact, it is only with the one- and two-electron systems, such as are found in H_2^+ , He and H_2 , respectively, that anything like satisfactory results have been obtained. It has been seen above that the energy equations for three- and four-electron systems are made up of terms which can be identified with the coulombic and exchange energies between electron pairs, and hence it is worth while to consider the two-electron system in molecular hydrogen. Certain results obtained in this case are assumed, as a rough approximation, to be applicable to other instances.

The Hydrogen Molecule.²¹—In the molecule of hydrogen, there are two atoms, each with a 1s-electron; if the wave functions of these electrons, exclusive of spin, are represented by a and b , for the first and second nucleus, respectively, then the four combinations of spin lead to four possible eigenfunctions.

	Total spin
$\Psi_{\text{I}} = (a\alpha)(b\beta)$	0
$\Psi_{\text{II}} = (a\beta)(b\alpha)$	0
$\Psi_{\text{III}} = (a\alpha)(b\alpha)$	1
$\Psi_{\text{IV}} = (a\beta)(b\beta)$	-1

²¹ Heitler and London, Ref. 10; Slater, Ref. 11.

These four functions presumably correspond to a singlet and a triplet level, for these require the total spins to be 0 and 1, 0, -1, respectively. Since there are no matrix components between states with different spins, it is evident that Ψ_{III} and Ψ_{IV} can be treated as individuals, whereas Ψ_{I} and Ψ_{II} are combined together. By means of the arguments presented above (pages 67ff.), it follows that

$$H_{\text{I,I}} \equiv \int \Psi_{\text{I}} \mathbf{H} \Psi_{\text{I}} d\tau = (ab)|H|(ab) \quad (210)$$

$$H_{\text{II,II}} \equiv \int \Psi_{\text{II}} \mathbf{H} \Psi_{\text{II}} d\tau = (ab)|H|(ab), \quad (211)$$

where $(ab)|H|(ab)$ is written for $\int (a_1 b_2) \mathbf{H} (a_1 b_2) d\tau$. These matrix components involve coulombic terms only. If the eigenfunctions a and b are normalized, then

$$\Delta_{\text{I,I}} \equiv \int \Psi_{\text{I}} \Psi_{\text{I}} d\tau = 1 \quad (212)$$

and

$$\Delta_{\text{II,II}} \equiv \int \Psi_{\text{II}} \Psi_{\text{II}} d\tau = 1. \quad (213)$$

Further,

$$H_{\text{I,II}} = H_{\text{II,I}} = -(ab)|H|(ba), \quad (214)$$

and

$$\Delta_{\text{I,II}} = \Delta_{\text{II,I}} = -(ab)|1|(ba) = S^2, \quad (215)$$

where $(ab)|H|(ba)$ is the exchange integral $\int (a_1 b_2) \mathbf{H} (a_2 b_1) d\tau$ and $(ab)|1|(ba)$ is the corresponding matrix component of unity, i.e., $\int (a_1 b_2) (a_2 b_1) d\tau$, which has been denoted by the symbol S^2 . The secular equation for the energies of the states I and II, as given by the variation method, or by the first-order perturbation calculation, is

$$\begin{array}{ccc} H_{\text{I,I}} - \Delta_{\text{I,I}} E & H_{\text{I,II}} - \Delta_{\text{I,II}} E & \\ & & = 0, \end{array} \quad (216)$$

$$H_{\text{II,I}} - \Delta_{\text{II,I}} E \quad H_{\text{II,II}} - \Delta_{\text{II,II}} E$$

which reduces to

$$\begin{array}{ccc} H_{\text{I,I}} - E & H_{\text{I,II}} - S^2 E & \\ & & = 0, \end{array} \quad (217)$$

$$H_{\text{I,II}} - S^2 E \quad H_{\text{II,II}} - E$$

where $H_{\text{I,I}}$, $H_{\text{II,II}}$, $H_{\text{I,II}}$ and S^2 have the significance given above. The two solutions of this equation are

$$E_1 = \frac{H_{I,I} + H_{I,II}}{1 + S^2} \quad (218)$$

and

$$E_2 = \frac{H_{I,I} - H_{I,II}}{1 - S^2}. \quad (219)$$

It may be noted that the solutions of the two first-order secular equations involving Ψ_{III} and Ψ_{IV} are identical with (219), so that E_2 must be the energy of the triplet state and E_1 that of the singlet. From what has been already said (page 73) it will be clear that $H_{I,I}$ is the coulombic integral, whereas $H_{I,II}$ is the exchange (resonance) integral; hence, Eqs. (218) and (219) can be written in a form analogous to that of (205), *viz.*,

$$E = \frac{A \pm \alpha}{1 \pm S^2}, \quad (220)$$

where A and α are the coulombic and exchange (resonance) energies, respectively. If S^2 were zero, as would be the case if the eigenfunctions were orthogonal and as was assumed in the deduction of Eq. (205), then (220) would become identical with

the form to which (205) reduces when the electrons c and d are removed to infinity, *i.e.*, when the β 's and γ 's are all zero.

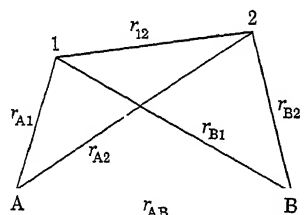


FIG. 5.—Distances in the hydrogen molecule between the nuclei (A and B) and the electrons (1 and 2).

For the evaluation of E_1 and E_2 , it is necessary to know the Hamiltonian operator for the system of two hydrogen atoms, *i.e.*, two atoms and two nuclei, and also the eigenfunctions a_1b_2 and a_2b_1 [*cf.* Eqs. (210), (211), (214) and (215)]. The former,

neglecting the terms for nuclear interaction, is readily found, from Eq. (176), to be

$$\frac{\hbar^2}{8\pi^2m} (\nabla_1^2 + \nabla_2^2) - (V_A + V_B) + V_0, \quad (221)$$

where ∇_1^2 and ∇_2^2 are the Laplacian operators with respect to the coordinates of electrons 1 and 2, respectively, and

$$V_A = \frac{\varepsilon^2}{r_{A1}} + \frac{\varepsilon^2}{r_{A2}}; \quad V_B = \frac{\varepsilon^2}{r_{B1}} + \frac{\varepsilon^2}{r_{B2}}; \quad V_0 = \frac{\varepsilon^2}{r_{AB}} + \frac{1}{r_{12}} \quad (222)$$

The various r values are shown in Fig. 5, where A and B are the two hydrogen nuclei and 1 and 2 the electrons.

The eigenfunctions a_1b_2 and a_2b_1 are taken as equal to the product of the orbital functions for 1s-electrons of the hydrogen atom, *viz.*, $(\pi a_0^3)^{-1/2}e^{-r/a_0}$, where r is the distance from the electron to the nucleus and a_0 is the radius of the normal Bohr orbit, *i.e.*, $\hbar^2/4\pi^2m\epsilon^2 = 0.53 \text{ \AA.}$; thus,

$$a_1b_2 = \frac{1}{\pi a_0^3} e^{-(r_{A1}+r_{B2})/a_0}, \quad (223)$$

and

$$a_2b_1 = \frac{1}{\pi a_0^3} e^{-(r_{A2}+r_{B1})/a_0}. \quad (224)$$

In the first case the electron 1 is assumed to be associated with the nucleus A and 2 with B. In the second case the electrons are reversed.

Proportions of Coulombic and Exchange Energies.—By introducing the four Schrödinger wave equations for the two electrons each associated with either of the two nuclei, *viz.*,

$$\nabla_1^2 a_1 + \frac{\hbar^2}{8\pi^2m} \left(E_0 + \frac{1}{r_{A1}} \right) a_1 = 0, \quad (225)$$

and similar equations for the orbitals b_1 , a_2 and b_2 , where E_0 is the energy of the hydrogen atom, it is possible, in principle, to calculate E_1 and E_2 from Eqs. (218) and (219), for various internuclear distances. In practice, however, it is necessary to evaluate a number of complicated integrals. The first successful attempt at this task, following the original work of Heitler and London, was that of Y. Sugiura.²² From his equations, it is possible to determine $E_1 - 2E_0$ and $E_2 - 2E_0$ as functions of r_{AB} . Since $2E_0$ is the energy of two separated hydrogen atoms, these quantities represent the potential energies, with respect to the constituent atoms, of two possible forms of the hydrogen molecule. By taking the energy of the separated atoms as the arbitrary energy zero, the results give the actual values of E_1 and E_2 ; and since S^2 is known in terms of the internuclear distances, the separate coulombic and exchange (resonance) energies can be calculated. The results obtained in this manner

²² Y. Sugiura, *Z. Physik*, **45**, 484 (1927).

are shown in Fig. 6.²³ It is found, in the first place, that the stable form of molecular hydrogen is the singlet state whose energy is given by E_1 . The triplet state, for which there is spectroscopic evidence, is always unstable with respect to hydrogen atoms. In the second place, it will be noted that the minimum in the potential-energy curve for the singlet state occurs when the internuclear separation is 0.80 \AA. , and the negative potential energy is 74 kcal. These figures should represent the equilibrium internuclear distance and the energy of dissociation of molecular hydrogen, respectively. The results are in fair agreement with the experimental data, 0.74 \AA. and 108.9 kcal.

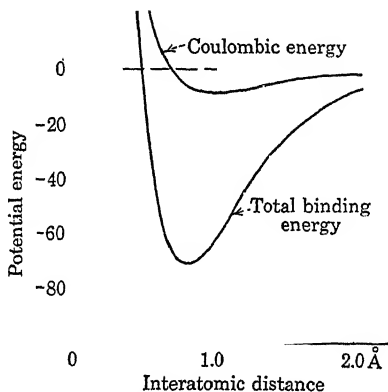


FIG. 6.—Total and coulombic binding energies for the singlet state of H_2 . (Eyring and Polanyi, from Sugiura's equations.)

An examination of Fig. 6 also shows that, at interatomic distances greater than about 0.8 \AA. , the coulombic energy constitutes a small proportion only of the binding energy of the hydrogen molecule. It appears, therefore, that two hydrogen atoms are held together, to a very large extent, by the so-called exchange, or resonance, energy. The fraction of the total binding energy that is coulombic apparently depends on the internuclear distances. The curve in Fig. 7 shows the variation with the distance between the atoms in a hydrogen molecule of ρ , where

$$\rho = \frac{\text{coulombic energy}}{\text{total binding energy}}, \quad (226)$$

²³ H. Eyring and M. Polanyi, *Z. physik. Chem.*, B, 12, 279 (1931).

calculated from Sugiura's equations. Provided that the interatomic distance exceeds about 0.8 \AA ., the coulombic energy appears to be between 10 and 15 per cent of the total binding energy of the hydrogen molecules; *i.e.*, $A/(A + \alpha)$ in Eq. (220) is approximately 0.1 to 0.15. The question arises, in order to facilitate the solution of Eqs. (206) and (209), whether the same ratio may be supposed to hold for $A/(A + \alpha)$, $B/(B + \beta)$, $C/(C + \gamma)$, etc., in these equations. The assumption will, indeed, be made in Chap. III that this fraction is approximately constant for a number of diatomic molecules, but it is important to realize its approximate nature.

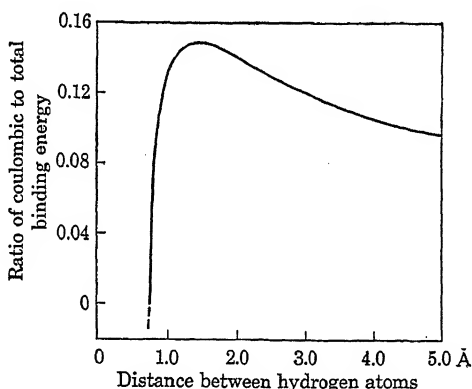


FIG. 7.—Proportion of coulombic energy for the H_2 molecule. (*Hirschfelder and Daniels.*)

It will be seen from Fig. 7 that ρ decreases rapidly as the hydrogen atoms are brought up to their equilibrium positions, and at a certain point Fig. 6 shows that the coulombic energy is zero, so that all the binding energy will be of the exchange type. This phenomenon is probably inevitable because the repulsion due to the coulombic term will set in before that brought about by the exchange contribution. It is possible, however, that the internuclear distance at which this occurs is much smaller than is given by Sugiura's equations; for, as seen above, the latter yield only approximately correct values for the dissociation energy and equilibrium separation of the atoms in molecular hydrogen. It may be mentioned that some writers²⁴ have cast doubt on the significance of the exchange energy, which has been

²⁴ A. S. Coolidge and H. M. James, *J. Chem. Phys.*, **2**, 811 (1934).

assumed to constitute such an important part of the total binding energy. By using suitable eigenfunctions, it is possible to derive by means of the variation treatment a value for the energy of the hydrogen molecule in close agreement with that obtained experimentally, and yet the calculation contains nothing resembling the exchange integrals of the type considered above.²⁵ It must be pointed out, however, that, if this criticism were valid for the hydrogen molecule, it would be applicable to the many problems of structural chemistry in which the concept of resonance has proved so valuable.

Admitting, for the present, that the exchange energy, or resonance energy, constitutes an important part of the total binding energy, it is necessary to determine whether the proportion, calculated by the Heitler-London theory and Sugiura's equations, is the same for all diatomic molecules. It appears clearly established that the fraction ρ in Eq. (226) increases with increasing principal quantum number n of the s -electrons. The coulombic energy remains almost constant, but the resonance energy diminishes rapidly as n increases. The approximate values of ρ calculated for various principal quantum numbers, for atomic separations exceeding the respective equilibrium values for diatomic molecules, are recorded in Table IV.²¹

TABLE IV.—PROPORTION OF COULOMBIC ENERGY FOR DIFFERENT QUANTUM NUMBERS

n	1	2	3	4
ρ	0.12	0.22	0.32	0.40

It should be noted that the data quoted above refer to a bond formed by two s -electrons. If two p -electrons are concerned, the results are quite different. It appears that under these conditions the coulombic contribution is by far the more important and that the exchange energy is relatively small.²⁷

²⁵ H. M. James and A. S. Coolidge, *ibid.*, **1**, 825 (1933).

²⁶ J. H. Bartlett and W. H. Furry, *Phys. Rev.*, **38**, 1615 (1931); N. Rosen and S. Ikehara, *ibid.*, **43**, 5 (1933).

²⁷ J. H. Bartlett, *ibid.*, **37**, 507 (1931).

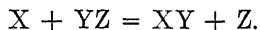
CHAPTER III

POTENTIAL-ENERGY SURFACES

It is now generally accepted that nearly all processes taking place at a definite rate, and chemical reactions in particular, are associated with an energy of activation representing the minimum energy the system must acquire before it can undergo the appropriate change. In the present chapter an attempt will be made to obtain some indication of the fundamental significance of the energy of activation and the nature of the activated state with special reference to chemical changes involving three or four atoms.

ENERGY OF ACTIVATION

Potential-energy Curves and the Activated State.—Consider a reaction involving the atom X and the molecule YZ, *viz.*,



The atoms Y and Z in YZ are joined by a single bond, *i.e.*, by a pair of electrons with opposite spins; the atom X is supposed to have an uncoupled electron. As X is brought up to YZ, the interaction of the three electrons causes a decrease in the exchange energy, with the result that the attraction between Y and Z is diminished and the atoms will tend to separate. The continued approach of X to YZ is thus accompanied by an increase in the potential energy of the system due to the increasing repulsion of X by YZ and the decreasing attraction of Y and Z. Finally, a point is reached at which the atom Z commences to be repelled and the system attains the condition in which the reaction $X + YZ = XY + Z$ can take place. If X is brought still closer to Y, so that the distance between them becomes the normal interatomic separation, the atom Z is repelled, and the potential energy of the system decreases. The variation of potential energy during the course of the change may be represented qualitatively by moving from left to right along a curve

such as is shown in Fig. 8. It is evident that before the system $X + YZ$ can become $XY + Z$, *i.e.*, before the reaction under consideration can occur, the reactants must acquire the energy represented by the maximum of the curve. This conclusion may be stated in the figurative form that the reacting system must "surmount an energy barrier." The difference in energy between the initial state and the maximum of the curve, *i.e.*, the top of the barrier, is then the energy of activation (E) of the

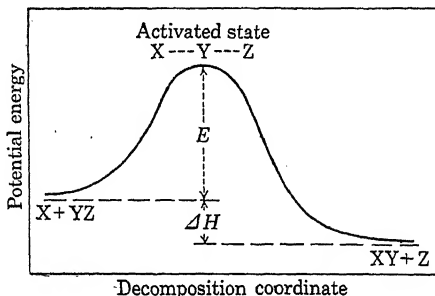


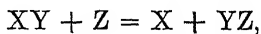
FIG. 8.—Variation of potential energy accompanying the reaction $X + YZ = XY + Z$.

process. The configuration of $X-Y-Z$ at the maximum is called the "activated state" or "activated complex" of the reaction; in this condition the atoms are so disposed with reference to one another that Y can become associated either with X or with Z , and a very slight displacement will result either in reaction to form XY and Z or in return to the initial state.

The potential-energy curve depicted in Fig. 8 may also be used in considering the reverse reaction



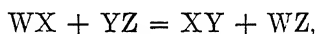
The activated state is the same as for the reaction between X and YZ , so that the same energy barrier has to be crossed; the height of the top of the barrier above the initial state is now $E + \Delta H$ where ΔH is the difference in heat content between XY and Z on the one hand and X and YZ on the other, *i.e.* the heat of reaction at constant pressure.* It will be evident from Fig. 8 that in an endothermic process, such as



* This result is applicable when reaction rates are measured in terms of pressure units; if concentration units are employed, then ΔH must be replaced by ΔE , the increase of internal energy.

the energy of activation must be at least equal to the heat absorbed in the reaction. This accounts for the fact that endothermic reactions generally have relatively high energies of activation and hence are, on the whole, slow in comparison with exothermic reactions.

Chemical Reactions as an Electron Problem.—The foregoing discussion of the mechanism of activation is based essentially on the views of F. London,¹ who suggested that many chemical reactions are “adiabatic”* in character and that Eqs. (206) and (209) developed in Chap. II for four- and three-electron problems, respectively, could be utilized to evaluate, approximately, the potential energy of a system of three or four reacting atoms for various interatomic distances. Suppose the atoms W and X in a molecule WX are joined by a single bond formed by the two *s*-electrons, and suppose also that the same type $\sigma_{\frac{1}{2}}$ bond exists in another molecule YZ which reacts with WX, thus,



the products XY and WZ also having similar single bonds. Since there is no change in the quantum numbers of the four valence electrons concerned in the process, the potential-energy change during the course of the reaction may be regarded as due to the rearrangement of the four *s*-electrons. In exactly the same manner, it can be seen that the reactions between X and YZ is essentially one concerning three *s*-electrons; hence, the change in potential energy accompanying the approach of X to YZ and the final expulsion of Z can be treated as a three-electron problem.

Three-atom Systems.—Suppose the three atoms X, Y and Z taking part in the reaction $X + YZ = XY + Z$ are disposed in the general manner shown in Fig. 9, where r_1 , r_2 and r_3 are the distances between X and Y, Y and Z and X and Z, respectively. If r_2 and r_3 are made very large, *i.e.*, if Z is removed to a

¹ F. London, “Probleme der modernen Physik (Sommerfeld Festschrift),” p. 104, 1928; *Z. Elektrochem.*, **35**, 552 (1929).

* An adiabatic change is one in which there is a continuous equilibrium between electrons and nuclei, there being no *abrupt* electronic rearrangement involving a jump from one electronic level to another; the whole process takes place on a single potential-energy surface. For an adiabatic reaction a single eigenfunction can be used to represent the state of an electron throughout the course of the reaction.

distance, the potential energy of the system will be equal to that of the molecule XY with the atoms separated by a distance r_1 . Let the energy in this state be $A + \alpha$, where A is the coulombic portion and α that due to exchange forces (page 78). Similarly, if X is removed to a distance, $B + \beta$ gives the corresponding energy of the molecule YZ, with the atomic separation equal to r_2 . With Y removed to infinity the potential energy of XZ, when the atoms are r_3 apart, is $C + \gamma$. From the results obtained in Chap. II it follows,* therefore, that for the given

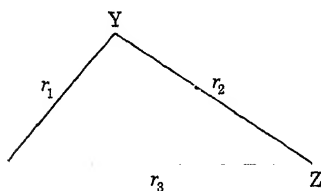


Fig. 9.—System involving three atoms.

atomic separation, the potential energy of the system X, Y and Z, with reference to the energy of the separated atoms as zero, is

$$E = Q - \left\{ \frac{1}{2} [(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2] \right\}^{1/2}, \quad (1)$$

where Q is the sum of the coulombic energies, *i.e.*, $A + B + C$. If A and α , B and β and C and γ are known or can be calculated for the three molecules XY, YZ and XZ, for various interatomic distances, as is the case with the hydrogen molecule (page 81), it should be possible to evaluate E for all possible configurations of the three atoms X, Y and Z. If there is no restriction on the values of r_1 , r_2 and r_3 , which vary independently, it would require a four-dimensional figure to represent the results diagrammatically; fortunately, it is possible to introduce a simplification based on the fact, which will be proved later, that the system X, Y, Z has the lowest potential energy when the three atoms are in a straight line.† In other words, the activation energy is least when X approaches YZ along the line joining the atoms Y and Z, and hence this must be the configuration of the three atoms by which the reaction mainly occurs. It is for the condition

* Strictly speaking, Eqs. (206) and (209), pp. 76 and 77, give the sum of the kinetic and potential energies of the electrons; in view of the almost stationary nature of the nuclei, these equations may be regarded as giving the potential energies of the systems of three and four atoms, respectively. In any case the difference in energies for various internuclear separations, which is important from the standpoint of activation energy, is the difference in potential energies.

† This is true for *s*-electrons but may not hold if *p*-electrons are involved (*cf.* p. 222).

represented in Fig. 10 that the energy of the system will, therefore, be calculated. It is apparent that r_3 is the sum of r_1 and r_2 , so that there are only two distances which can vary independently. The representation of the variation of the potential energy with interatomic distance now requires a three-dimensional model, and the result is called a "potential-energy surface." For practical purposes, however, it is more convenient to draw a contour diagram in which the various contour lines pass through points representing configurations having the same energy; such diagrams are, nevertheless, often referred to as potential-energy surfaces.

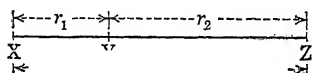


Fig. 10.—Linear system of three atoms.

The process of evaluating the potential energy as given by Eq. (1) can be greatly simplified by means of the following

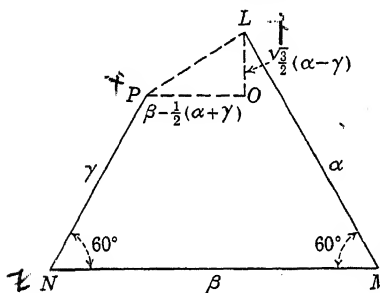


Fig. 11.—Graphical determination of resonance energy contribution. (Altar and Eyring.)

graphical construction which, it must be emphasized, is independent of the configuration of the atoms.² Let the lengths of the lines LM , MN and NP which make angles of 60° with each other, be proportional to the values of the exchange energies α , β and γ , respectively: draw LO perpendicular to NM and PO perpendicular to LO . It can be readily shown that LO is equal to $\frac{1}{2} \sqrt{3} (\alpha - \gamma)$ and PO is $\beta - \frac{1}{2}(\alpha + \gamma)$, so that PL is

$$(\alpha^2 + \beta^2 + \gamma^2 - \alpha\beta - \beta\gamma - \alpha\gamma)^{\frac{1}{2}},$$

which is identical with the term

$$\left\{ \frac{1}{2} [(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2] \right\}^{\frac{1}{2}}$$

in Eq. (1), and thus represents the resonance-energy contribution to the system of three atoms.* In order that PL may have the largest possible value, for given values of LM and NM , compatible with the type of construction shown in Fig. 11, NP must be small; the exchange energy γ for the atoms X and Z

² W. Altar and H. Eyring, *J. Chem. Phys.*, **4**, 661 (1936).

* The construction of Fig. 11 and the evaluation of PL can be expedited by the use of sliding rulers (J. O. Hirschfelder and F. Daniels, unpublished).

should therefore be small. This condition is obtained when the distance r_3 between X and Z is as great as possible, for given values of r_1 and r_2 , *i.e.*, when X is on the straight line passing through Y and Z. It follows, therefore, that the resonance energy for the whole system has its largest value when the configuration of the three atoms is linear. Corresponding to the small γ there will also be a decrease in the numerical value of the coulombic energy C , but this is of much lower magnitude. The net result of the linear configuration is to make the potential energy of the system have its lowest, *i.e.*, largest negative, value. It follows, therefore, that in the reaction between X and YZ the lowest energy barrier, corresponding to the activated state,

will be realized when X approaches YZ along the line joining the centers Y and Z.

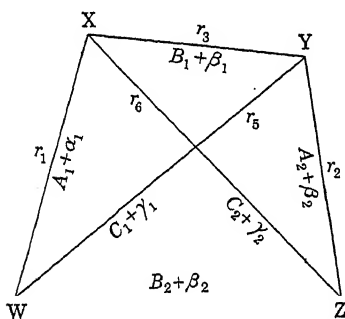


FIG. 12.—System involving four atoms.

Four-atom Systems.—A system of four atoms W, X, Y and Z may be represented as in Fig. 12 where the four are not necessarily all in one plane. As before, the energies of the individual diatomic molecules WX, YZ, XY, WZ, WY and XZ are seen to be $A_1 + \alpha_1$, $A_2 + \alpha_2$, $B_1 + \beta_1$, $B_2 + \beta_2$, $C_1 + \gamma_1$ and $C_2 + \gamma_2$,

respectively. As shown on page 76 the equation for the potential energy due to the interaction of the *s*-electrons of all four atoms when brought together will be given by an equation identical with Eq. (1) except that Q is given by

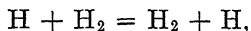
$$Q = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 \quad (2)$$

and α stands for $\alpha_1 + \alpha_2$, β for $\beta_1 + \beta_2$ and γ for $\gamma_1 + \gamma_2$. It is apparent that, bearing in mind the altered significance of the quantities α , β and γ , exactly the same geometrical construction as was used for three atoms (see Fig. 11) may be employed to evaluate the exchange-energy contribution to the potential energy of the system. The argument that the distance PL in Fig. 11 should be a maximum for the activation energy to be a minimum applies equally here; and it can be readily seen that, for given values of $\alpha_1 + \alpha_2$ and $\beta_1 + \beta_2$, the sum of the exchange energies $\gamma_1 + \gamma_2$ will

be a minimum when the distances r_5 and r_6 in Fig. 12 are as large as possible for particular values of r_1 , r_2 , r_3 and r_4 . This condition will arise when all four atoms are in one plane; hence, it may be assumed that in the reaction $WX + YZ = YX + WZ$, involving s-electrons, a planar activated state will occur more frequently than any other, and the energy of this configuration may be used to calculate the activation energy of the reaction.

CONSTRUCTION OF POTENTIAL-ENERGY SURFACES

The Semi-empirical Method.³—The first attempts to plot potential-energy surfaces and hence to calculate activation energies from molecular and atomic properties were made by H. Eyring and M. Polanyi who examined the relatively simple process



representing the conversion of para- to ortho-hydrogen brought about by hydrogen atoms. In order to evaluate E by Eq. (1), the first requirement is obviously to know how the binding energies of the separate diatomic molecules, represented by the formulae XY , XZ and YZ , are divided into their coulombic and exchange (resonance) contributions for various atomic separations. In the particular reaction under consideration, each of these molecules is H_2 , and it appeared possible that the values of the two kinds of energy could be obtained from Sugiura's solution of the Heitler-London integrals (see page 81 and Fig. 6); the results were, however, not satisfactory. This is not surprising; for not only is Eq. (1) itself approximate, but, as seen on page 82, Sugiura's equations give a value for the heat of dissociation of molecular hydrogen that is about 35 kcal. smaller than the experimental value. After considering various possibilities, Eyring and Polanyi developed the following procedure which has become known as the "semi-empirical method." The total potential energy of a diatomic molecule, with reference to the energy of its constituent atoms, can be obtained from spectroscopic data; then, in most cases, the assumption is made that the coulombic energy is a constant fraction (ρ) of the total for the interatomic distances which are significant in the reaction,

³ H. Eyring and M. Polanyi, *Z. physik. Chem.*, **B**, **12**, 279 (1931). See also H. Eyring, *J. Am. Chem. Soc.*, **53**, 2537 (1931); **54**, 3191 (1932); *Chem. Rev.*, **10**, 103 (1932).

for all the molecules concerned. In some instances (*cf.* page 255), allowance is made for the variation of the fraction ρ with the distance between the atoms. Although such a variation does occur (page 83), it is generally small over the range of distances that are important for the reaction. The assumption of a constant fraction of coulombic energy is admittedly an approximation, but it will be seen in Chap. V that the activation energies calculated on the basis of different assumed proportions of coulombic energy do not vary greatly; hence, it seems unlikely that, except in special circumstances, the assumption can lead to serious errors, especially in the vicinity of the activated state.

It was mentioned above that the total energy of a diatomic molecule for different atomic distances can be derived from spectroscopic measurements. The most convenient method is to make use of the function proposed by P. M. Morse⁴ which gives the dependence of the binding energy E of a diatomic molecule on the distance r between the atoms, with reference to the energy of the separated atoms as zero; it is

$$E = D'[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}], \quad (3)$$

where D' is the heat of dissociation of the molecule *plus* the zero-point energy, r_0 is the equilibrium interatomic distance of the normal molecule and a is $0.1227\omega_0(\mu/D)^{1/2}$, the quantity ω_0 being the equilibrium vibration frequency and μ the reduced mass of the molecule. In general, both D' and ω_0 , which are expressed in wave numbers' (cm.^{-1}), as well as r_0 , are obtained from spectroscopic measurements; since these are known, it is possible to calculate the energy of the diatomic system for any separation of the two atoms. Provided that the requisite data are available for the three molecules XY, YZ and XZ, it is possible to determine the quantities $A + \alpha$, $B + \beta$ and $C + \gamma$ for any particular values of r_1 , r_2 and r_3 by means of the appropriate form of Eq. (3). As explained above, the assumption is now made that the coulombic energy is a certain fraction of the total binding energy, and so A , B and C and α , β and γ are obtained separately. By means of Eq. (2), together with the simple geometrical device illustrated in Fig. 11, or by the use of the equivalent sliding rulers, the potential energy of the system can be readily calculated for a given value of r_1 and r_2 . This procedure is repeated until

⁴ P. M. Morse, *Phys. Rev.*, **34**, 57 (1929).

sufficient points are obtained for the potential-energy contour diagram to be plotted; since it is the region in the vicinity of the activated state that is of particular interest, it is the usual practice to calculate the energies for interatomic distances between about 0.5 and 4 Å.

Simplified Potential-energy Surfaces.⁵—Some of the main features of a potential-energy surface may be made evident in a relatively simple manner by considering only configurations in which the distance between the atoms Y and Z in the molecule YZ are kept constant while the distance between X and Z is diminished. The potential energy can then be expressed as a function of one coordinate, *viz.*, the X—Z distance. Suppose, for example, that in the reaction between atomic and molecular hydrogen, leading to the para-ortho conversion, the two atoms in the hydrogen molecule are held in the positions they occupy in the normal state and a third hydrogen atom is brought up to them from various directions. The potential energies may be calculated, as described above, and a series of contour lines of constant potential energy for the system of these atoms can be plotted. The result obtained on the assumption that the coulombic energy is 20 per cent of the total binding energy is shown in Fig. 13.* An atom of hydrogen coming up to the molecule from a great distance, in any direction, will be attracted at first by the van der Waals forces; but as it comes into the region shown in the diagram the attraction changes to repulsion. A hydrogen atom will have average energy in one direction not exceeding kT , and at room temperature this will amount to somewhat less than 1 kcal. per mole. It follows, therefore, that as an average hydrogen atom approaches a hydrogen molecule the former will commence to reverse its direction of motion when its center is approximately at a distance from the latter represented by the 1-kcal. contour line. The “kinetic theory shell” of the hydrogen molecule is thus, approximately, in the position shown in Fig. 13. The effective “collision” diameter of the molecule would thus be about 3 Å, at ordinary temperatures.

⁵ J. O. Hirschfelder, H. Eyring and B. Topley, *J. Chem. Phys.*, **4**, 170, (1936).

* Only half the contour diagram is shown in the figure, the lower half being exactly the mirror image of the upper; the whole potential-energy surface is, in fact, cylindrically symmetrical and has a plane of symmetry.

An atom having energy greater than the average will be able to approach more closely to the molecule, but it is clear from the diagram that this will be easiest if the atom advances along the line joining the two nuclei of the molecule. This is another way of presenting the argument, given above, that the potential-energy barrier will be lowest when the three interacting atoms lie on a straight line.

It is of interest to follow the history of an atom approaching in this most favorable direction: the potential energy of the system is seen to increase gradually until a value of about 7.5 kcal. is reached, after which there is a fall, indicating a slight

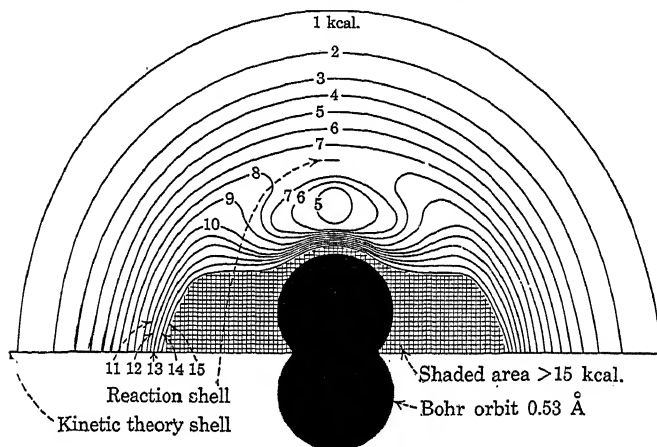


FIG. 13.—Potential-energy contours for approach of a hydrogen atom to a rigid hydrogen molecule. (*Hirschfelder, Eyring and Topley.*)

attraction. It is clear that only atoms possessing energy in excess of 7.5 kcal., the activation energy, will be able to advance close enough to the molecule of hydrogen to undergo some attraction. The position marked "reaction shell" represents the top of the energy barrier, and it is in this region that the activated state will exist. For the purpose of drawing Fig. 13, it was assumed that the distance between the atoms in the hydrogen molecule remains fixed; but in actual fact this is probably not the case (see, however, page 151). As the incoming atom approaches the "reaction shell," the two atoms in the molecule are forced apart, and consequently the activated state is formed, which may be represented as $\text{H} \cdots \text{H} \cdots \text{H}$, in which the central atom is just as likely to unite with the one to the left

as the one to the right. It will be noted that the contour lines in the diagram indicate a small depression in the vicinity of the activated state, the rim being at about 7.5 kcal. and the bottom at something less than 5 kcal. of energy. This basinlike depression at the top of the barrier is a common feature of potential-energy surfaces, and its significance will be considered more fully at a later stage.

The equipotential lines for the approach of a chlorine atom to a molecule of hydrogen, with fixed interatomic distance, are

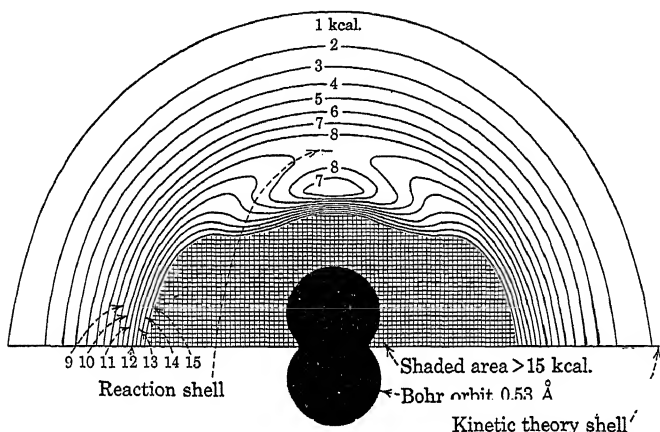


FIG. 14.—Potential-energy contours for approach of a chlorine atom to a rigid hydrogen molecule. (Hirschfelder, Eyring and Topley.)

depicted in Fig. 14. The general conclusions to be drawn are similar to those described in connection with the reaction between atomic and molecular hydrogen and need not be discussed further. The diameter of the "kinetic theory shell" is 4 to 5 Å., and the apparent activation energy is 8.5 kcal.

Complete Potential-energy Surface.⁶—The next step in the examination of potential-energy surfaces is to consider the case in which there is no restriction concerning the distance between the two atoms in the molecule YZ. In order to realize the most favorable conditions for the reaction, however, it is necessary that X should approach YZ along the line of centers; *i.e.*, X, Y and Z should lie on a straight line. By use of the methods

⁶ Eyring and Polanyi, Ref. 3; Eyring, Ref. 3; see also, *idem*, *Trans. Faraday Soc.*, **34**, 3 (1938); E. Wigner, *ibid.*, **34**, 29 (1938).

described on page 91 and on the assumption that the coulombic energy is a constant fraction of the total energy, for various interatomic distances, obtained from the appropriate Morse equation, the potential energy of the system is calculated for a series of values of r_1 and r_2 . The results are then plotted on a contour diagram with r_1 , *i.e.*, the X—Y distance, as abscissa and r_2 , *i.e.*, the Y—Z distance, as ordinate, the various contour lines passing through points of equal energy. For the present the two axes will be taken at right angles, and the type of diagram

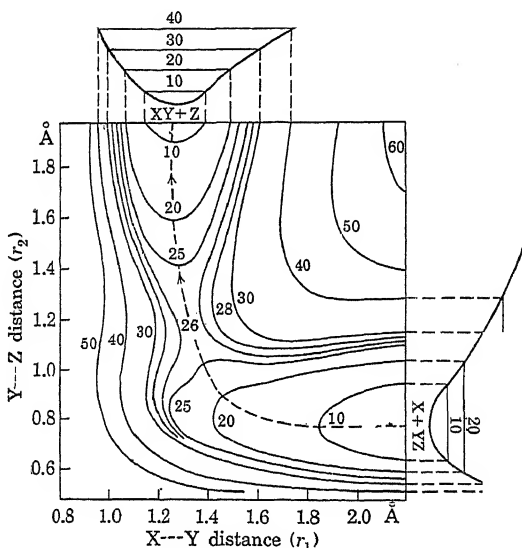
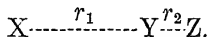


FIG. 15.—Typical potential-energy surface for a three-atom reaction.

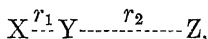
obtained is shown in Fig. 15; it is seen to consist of two valleys, each parallel to one of the axes, separated by a pass shaped somewhat like a saddle. At the top of the pass, called the “saddle point,” there is sometimes a shallow basin with gaps leading to the respective valleys. A section through the diagram parallel to the r_1 axis at large values of r_2 gives the normal potential-energy curve for the diatomic molecule X—Y; a similar section parallel to the r_2 axis will show the dependence of the potential energy of YZ on the atomic separation Y—Z.

The lower right-hand portion of Fig. 15 represents the energy of the reactants, since Y and Z are then at their normal

distances apart but X is far away from Y, *i.e.*, r_2 is small and r_1 large.



The final state, with r_1 small and r_2 large, *i.e.*,



is thus seen to be at the top left-hand corner of the diagram. It is evident that in the course of the reaction $\text{X} + \text{YZ} = \text{XY} + \text{Z}$, the system must pass from the lower right-hand corner to the upper left-hand one of the potential-energy surface. The path requiring the least energy is clearly indicated by the broken line; the system passes up the bottom of the "horizontal," or "east-to-west," valley, through the gap at the top of the pass, into the shallow basin, then out of the basin at the other gap and finally down the "vertical," or "north-to-south," valley. By following the

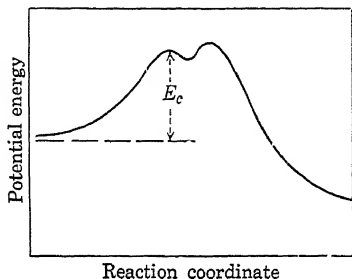


FIG. 16.—Profile of reaction path, showing shallow basin at the top of the barrier; E_c is the "classical" activation energy.

reaction path, *i.e.*, the broken line, in Fig. 15, it is possible to obtain an indication of the relative positions of the three atoms during the course of the reaction. As X is brought up to YZ, the distance between Y and Z is seen to be hardly affected at first; but as X comes closer, the atoms Y and Z begin to be forced apart as a consequence of the repulsive forces between X and Z, which now become appreciable. When the activated state is reached, at the top of the energy pass, the distance between X and Y is comparable with that between Y and Z, so that Y will be in a position to attach itself either to X or to Z. If it combines with Z, then reaction occurs. If the profile of the path were drawn in one plane, it would look something like that in Fig. 16; and, without going into the corrections necessitated by consideration of zero-point energies, the so-called "classical" energy of activation* of the process would be represented by the

* The quantity that has been called the "classical" activation energy actually refers to 0°K.

height of the top of the pass above the level of the initial state (see page 86). Conventionally, potential-energy curves are generally represented qualitatively as in Fig. 17; the ends are turned up to indicate vibration of the nuclei, *i.e.*, the variation of potential energy with interatomic separation, in initial (left) and final (right) states. This type of diagram will be used frequently throughout this book, the ordinate being the potential energy and the abscissa described as the "reaction coordinate"; the latter is virtually the reaction path drawn in one plane.

Classical and Zero-point Activation Energies.—The London

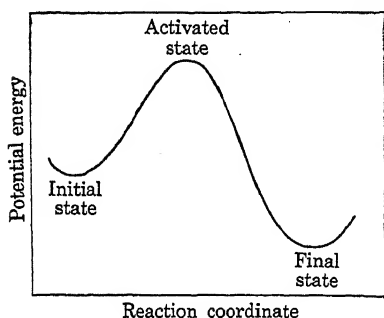


Fig. 17.—Potential-energy curve; conventional method of representing the variation of potential energy during the course of a reaction.

equation gives the potential energy of a system with respect to the energy of the separated atoms as zero, whereas the activation energy as generally quoted is the energy of the activated state with reference to the initial state; this point is illustrated diagrammatically in Fig. 18 for the reaction $X + YZ = XY + Z$. The potential energy of the activated state as given by Eq. (1) is repre-

sented by E ; and the so-called "classical" activation energy at the absolute zero, which is the difference between the potential energies of the lowest levels of the activated and initial states, without reference to zero-point energies, is E_c . It is seen that $E + E_c$ is numerically equal to D' , which is the heat of dissociation of YZ plus the zero-point energy (*cf.* page 92). The true activation energy at the absolute zero (E_0) is the difference between the lowest observed vibrational levels in activated and initial states, as shown in Fig. 18. The zero-point energy corresponding to any particular vibrational mode of frequency ν is approximately $\frac{1}{2}h\nu$ per molecule, where h is Planck's constant; hence, it follows, if there is no interaction between the various degrees of vibrational freedom, that

$$E_0 = E_c + \sum \frac{1}{2}h\nu_a - \sum \frac{1}{2}h\nu_i$$

where ν_a and ν_i represent the frequencies in activated and initial states, respectively. The vibrational modes of the reactants are

generally known, and those of the activated complex are derived from the potential-energy surface by the method to be described later in this chapter. It may be mentioned that the activation energies considered here are not quite the same as that obtained experimentally as described in Chap. I. The discrepancy, which depends on the difference in heat capacity of activated and initial states, is of a small order of magnitude and may be neglected for the present; it is considered more fully in Chap. IV.

Successive Reactions.—The study of successive reactions involves no new problems, since each stage has its own potential-

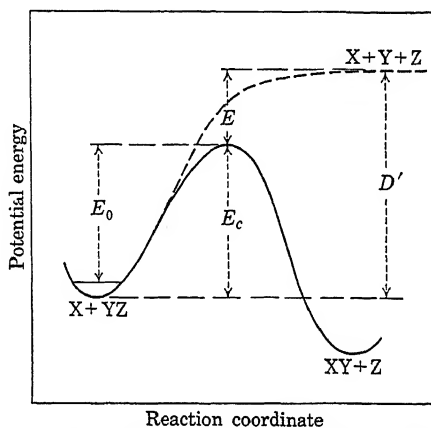


FIG. 18.—“Classical” and “true” activation energies. The zero-point energy in the activated state is not shown.

energy surface independent of the others. Certain points of special interest arise, however, from a consideration of the potential-energy curves. Suppose there are four successive stages, of which the third, for example, requires the highest activation energy; the potential-energy curve for the complete reaction will then be of the form shown in Fig. 19, the four potential barriers being represented by A , B , C and D . The activation energies for the separate reactions are E_A , E_B , E_C and E_D ; but the activation energy for the over-all reaction is E . This is the energy which the initial reactants R must acquire before they can surmount the highest barrier separating them from the final products P . The extents to which the intermediate products P_A , P_B and P_C are present at equilibrium is indicated by the difference in height between the equilibrium

potential energy for these substances and that of the reactant R. If the former, *e.g.*, for P_A , is less than the latter, so that the reaction, *i.e.*, $R \rightarrow P_A$, is exothermic, the equilibrium will favor the formation of an appreciable concentration of P_A . In other cases, *e.g.*, P_B , the amount of intermediate will be small. It may be noted that according to classical ideas the reaction under consideration would be expected to follow the complete path of the potential-energy curve, the various stages taking place in turn. The essential point emphasized in this book is, however, that the highest barrier must be surmounted before reaction takes place, and the presence of intermediate states is inconsequential

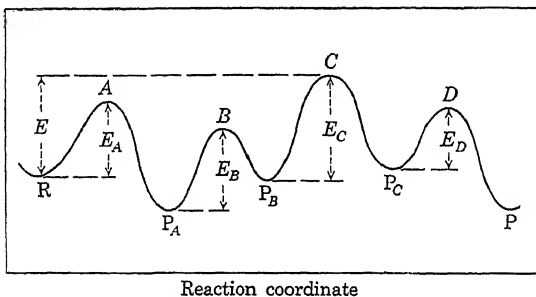


FIG. 19.—Potential-energy curve for successive reactions.

except in so far as such a state contains an appreciable fraction of the total molecules, which makes them really part of the initial state. It is possible for systems to pass over the highest barrier without necessarily having been through the intermediate states.

PROPERTIES OF POTENTIAL-ENERGY SURFACES

Diagonalization of Kinetic Energy.⁷—The potential-energy surface can be made to give information concerning the mechanics of the reaction, *i.e.*, the distribution of vibrational and relative translational energy in the system. By drawing the axes of the coordinates at an appropriate angle, so as to diagonalize the internal kinetic energy, the free frictionless motion, under the influence of gravity, of a particle, or mass point, sliding on the surface can be made to represent the analogous “motion” of the reacting system. The word “motion” here refers to the mutual transformations of kinetic and potential energies of the system, which can be compared with the analogous changes for

⁷ J. O. Hirschfelder, Dissertation, Princeton University, 1935.

a mass point sliding on an inclined surface. Strictly speaking, the cases are not quite comparable, for on the potential-energy surface the movement of the particle occurs in three dimensions, whereas the interatomic distances are plotted in the plane of the diagram. To make the agreement exact, it would be necessary to measure the distances along the actual surface, instead of in a plane; the discrepancy is not great and need not be considered further.

The simplest case to consider is that of a system of three atoms. In order that the potential-energy surface shall have the properties mentioned above, the essential condition is that the axes of the coordinates representing the distances between the atoms X and Y and between Y and Z should be skewed in such a manner that the kinetic energy of the mass point, when expressed in terms of the corresponding rectangular coordinates, is the sum of two square terms with no cross terms. That is, the kinetic energy should be expressible as $\frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\dot{y}^2$, where m is related to the mass of the system and x and y are rectangular coordinates corresponding to the actual coordinates on the potential-energy surface. Consider the general case of three particles of masses m_1, m_2, m_3 , lying on a straight line; the distance between m_1 and m_2 is r_1 , and the distance between m_2 and m_3 is r_2 , as shown in Fig. 20.



FIG. 20.—System of three particles lying on a straight line.

The internal kinetic energy T of the system relative to its center of mass is

$$T = \frac{1}{2} \cdot \frac{m_1 m_2}{m_1 + m_2} \dot{r}_1^2 + \frac{1}{2} \cdot \frac{(m_1 + m_2) m_3}{m_1 + m_2 + m_3} \left(\dot{r}_2 + \frac{m_1}{m_1 + m_2} \dot{r}_1 \right)^2, \quad (4)$$

where the first term is the energy of particles 1 and 2 with respect to each other and the second term is that of 1 and 2 combined with respect to 3. Upon multiplying out, Eq. (4) becomes

$$T = \frac{1}{2M} [m_1(m_2 + m_3)\dot{r}_1^2 + 2m_1 m_3 \dot{r}_1 \dot{r}_2 + m_3(m_1 + m_2)\dot{r}_2^2], \quad (5)$$

where $M = m_1 + m_2 + m_3$. Let the variables r_1 and r_2 be plotted on skewed axes, as shown in Fig. 21; then,

$$r_1 = x - y \tan \theta \quad (6)$$

and

$$r_2 = cy \sec \theta, \quad (7)$$

where x and y are the rectangular coordinates corresponding to r_1 and r_2/c , and c is a reduction factor. If these values for r_1 and r_2 are inserted in Eq. (5), it can be shown that if the cross terms, involving $r_1 r_2$, are to vanish, it is necessary that

$$\sin \theta = \frac{cm_3}{m_2 + m_3} \quad (8)$$

This gives the condition for diagonalization. Further, if the constant c is chosen so as to make the coefficients of \dot{x} and \dot{y} the same, which is the second condition necessary to make it

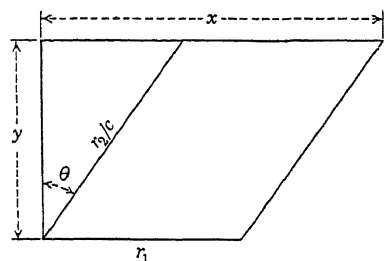


FIG. 21.—Construction of potential-energy surface with skewed coordinates.

possible to represent the system of three atoms by a ball sliding on a surface, then

$$c = \left[\frac{m_1(m_2 + m_3)}{m_3(m_1 + m_2)} \right]^{1/2}. \quad (9)$$

Hence, from Eqs. (8) and (9) it follows that

$$\sin \theta = \left[\frac{m_1 m_3}{(m_1 + m_2)(m_2 + m_3)} \right]^{1/2}. \quad (10)$$

With the values for c and $\sin \theta$ given by Eqs. (9) and (10), it is found that

$$T = \frac{1}{2} m \dot{x}^2 + \frac{1}{2} m \dot{y}^2, \quad (11)$$

where

$$m = \frac{m_1(m_2 + m_3)}{M}. \quad (12)$$

It is seen, therefore, that the condition which is being sought is given by Eqs. (9) and (10); the latter gives the angle through which the coordinates are skewed, and the former gives the reduction factor for plotting the sloping coordinate in terms of

r_2 . If m_1 , m_2 and m_3 are equal, as is the case for the reaction $\text{H} + \text{H}_2 = \text{H}_2 + \text{H}$, then θ is 30 deg. and the angle between the axes should be 60 deg. The factor c is unity, so that r_1 and r_2 may be plotted directly along the two axes. The only case where rectangular coordinates give the necessary conditions, *i.e.*, $\theta = 0$ deg., is when m_1/m_2 or m_3/m_2 is small. Unless m_1/m_3 is equal to unity, however, the reduction factor c will still be necessary. Thus rectangular coordinates are approximately applicable to the reaction $\text{H} + \text{Br}_2 = \text{HBr} + \text{Br}$, but the factor c is very different from unity.

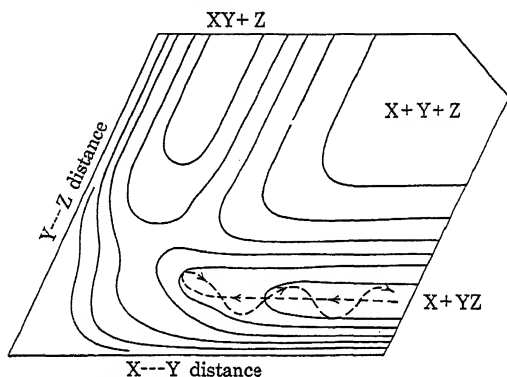


FIG. 22.—Interconversion of relative translational and vibrational energy.

Interconversion of Translational and Vibrational Energies.⁸—The diagonalized potential-energy surfaces obtained as described above can be utilized to give information of various kinds, and some of these will be considered first in a general manner, specific cases being discussed later. Suppose the mass point, or particle, representing the initial system $\text{X} + \text{YZ}$ is propelled directly along the bottom of the “east-west” valley from east to west. Since the system has no lateral motion, it will have at the commencement no vibrational energy but only translational energy of X relative to YZ . If there is comparatively little attraction between X and Y , the valley will rise steeply at the end; and if it has a slight curvature, as is generally the case, the particle will be reflected back, with a zigzag motion, *i.e.*, to and fro

⁸ H. Eyring, H. Gershinowitz and C. E. Sun, *J. Chem. Phys.*, **3**, 786 (1935); H. Gershinowitz, *ibid.*, **5**, 54 (1937); see also O. Oldenberg and A. A. Frost, *Chem. Rev.*, **20**, 99 (1937); E. Rabinowitsch, *Trans. Faraday Soc.*, **33**, 283 (1937).

across the valley (see Fig. 22). This means that under these conditions, as a result of the close approach, or "collision," of X and YZ , the translational energy of X is converted into vibrational energy of YZ . If the YZ molecule has some vibrational energy in the initial state, the path representing the interconversion of energy on collision will be of the form shown in Fig. 23. It should be noted that the paths indicated on the potential-energy surface are reversible, and so in the directions opposite to those represented by the arrows of Figs. 22 and 23 there is a conversion of vibrational to relative translational energy.

If there is considerable interaction between X and Y , so that the potential-energy diagram consists of two deep valleys with a

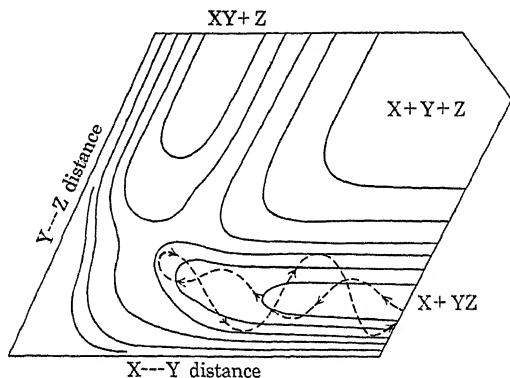


FIG. 23.—Interconversion of energy; system possessing some vibrational energy in addition to relative translational energy.

relatively low energy pass, representing the activated state in between, it is easily possible for a system $X + YZ$, with sufficient energy, moving up the "east-west" valley to pass over into the other valley, *i.e.*, to react. Nevertheless, owing to the shape of the surface in the vicinity of the activated state and to the initial distribution of energy in the $X + YZ$ system, there may be an interconversion of translational into vibrational energy with the result that although the total energy exceeds that necessary for activation the system is reflected back before it can reach the top of the pass. In other words, the system under these conditions has insufficient relative translational energy for X to come close enough to YZ for the activated state to be formed. It may be noted that if there is a considerable bend

in the valley beyond the saddle point representing the activated state, there is a possibility that the reacting system may be reflected back even after passing over the energy saddle; this is one of the factors sometimes responsible for the deviation of the transmission coefficient from unity.

Suppose, however, that the mass point representing the reacting system $X + YZ$ has sufficient energy to permit it to succeed in entering the valley representing the products $XY + Z$. It is evident that even if the energy was initially entirely translational in character, *i.e.*, the motion was parallel to the $X-Y$ distance axis, there will be a zigzag movement in the further valley showing that the excess translational energy of the reactant

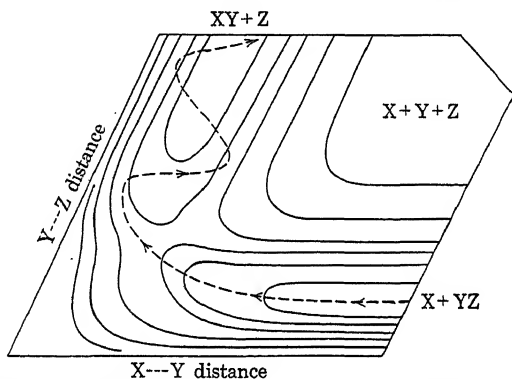


FIG. 24.—Excess translational energy of reactants converted into vibrational energy of resultants.

has been converted into vibrational energy of the product XY (Fig. 24). If the potential-energy surface has been constructed in the correct manner, the motion of a particle sliding on it will give a true representation of the behavior of the system. In actual practice the molecule of reactant YZ has some vibrational energy at the start; and provided that the particle is endowed with the equivalent to-and-fro movement, its motion will still give a true picture of the distribution of translational and vibrational energies in the reacting system. By reversing the procedure, it is possible to find the optimum proportions of the two forms of energy which the system should have initially in order that reaction may occur with the least expenditure of total energy. The mass point, initially at rest, *i.e.*, with zero relative translational and vibrational energies, is allowed to slide from

the saddle point representing the activated state down the "east-west" valley of the reactants. The extreme zigzag movement across the valley will indicate the required amount of vibrational energy, and the speed at the bottom gives the translational energy of X relative to YZ.

Combination of Atoms.—The removal of energy by a third body is of importance in reactions involving the combination of two atoms, and the potential-energy surfaces constructed in the

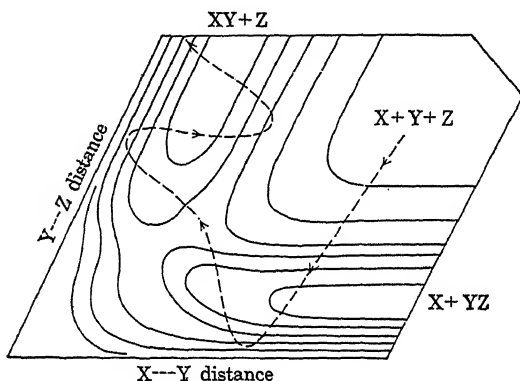
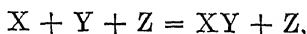


FIG. 25.—Atom-combination reaction; Y and Z are capable of interacting and so facilitate the combination of X and Y.

manner described above are of value in this connection. For the reaction



for example, the appropriate surface is the same as that for the reaction $X + YZ = XY + Z$ just discussed. The initial state is now the plateau at the "northeast" (top right) corner, and the final state is the (approximately) "north-south" valley, as before. If the mass point representing the reacting system were imagined to slide directly from the plateau into the valley, the to-and-fro motion would in general return it to the plateau and there would be no reaction. This is equivalent to saying that the third body Z does not remove the energy liberated in the formation of the molecule XY, and so the latter dissociates immediately. Further, if the system slid into the "east-west" valley approximately at right angles to the contour lines, the result would generally be similar. Only if the mass point leaves the plateau at a suitable angle, *i.e.*, with sufficient of both transla-

tional and vibrational energy, as shown in Fig. 25, enters the $X + YZ$ valley and then passes over into the $XY + Z$ valley, the translational energy being converted into vibrational, does the reaction leading to $XY + Z$ occur. It can be readily seen that the efficiency of Z in facilitating the combination of X and Y depends on the shape of the potential-energy curve. If Y and Z interact to an appreciable extent, the "east-west" valley will be deep and the ridge separating the two valleys will be relatively low, so that passage from one to the other will not be difficult. If, on the other hand, Y and Z do not attract each

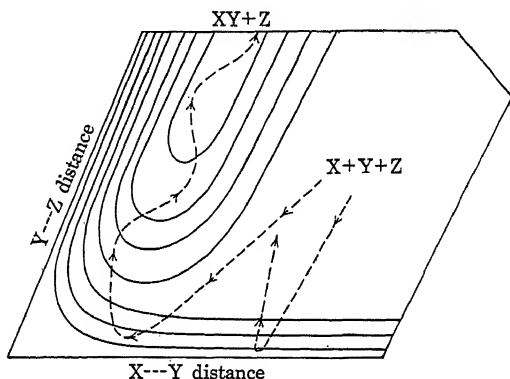
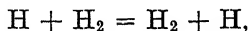


FIG. 26.—Atom-combination reaction; Y and Z do not interact to any appreciable extent. Reaction occurs only if the system enters the curved ("non-ruled") region of the surface.

other to any extent, the "east-west" valley will be shallow, and in fact the plateau may be regarded virtually as extending over the whole right-hand portion of the surface (Fig. 26). The probability of a system leaving the plateau and passing out through the "north-south" valley will be greatly decreased.

REACTIONS INVOLVING HYDROGEN ATOMS

The Para-ortho Hydrogen Conversion.⁹—The potential-energy surface for the reaction



i.e., the interconversion of the ortho- and para-forms of hydrogen, has been studied in some detail, and so it will be utilized to illustrate specifically the general arguments considered above. The surface which satisfies the conditions that a mass point

⁹ Eyring and Polanyi, Ref. 3; Hirschfelder, Eyring and Topley, Ref. 5.

sliding on it shall indicate the distribution of the relative translational and the vibrational energy in the system is shown in Fig. 27; it has been calculated on the assumption that 14 per cent of the binding energy is additive, *i.e.*, coulombic, in nature. The two valleys representing $H + H_2$ and $H_2 + H$, respectively, and the shallow basin, about 2.5 kcal. deep, at the top of the energy pass, are clearly seen. At the borders of the diagram the

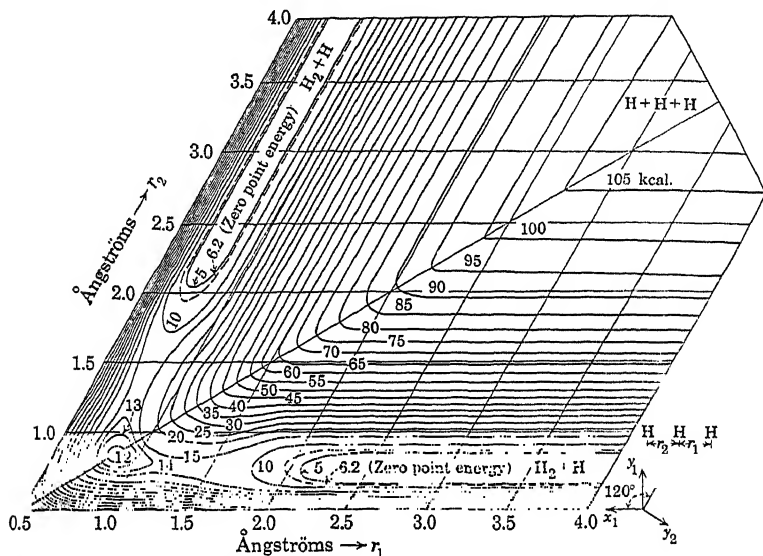


Fig. 27.—Potential-energy surface for the system of three hydrogen atoms based on 14 per cent coulombic energy. (Eyring, Gershinowitz and Sun.)

valleys rise steeply, corresponding to the repulsion between two hydrogen atoms forced closer together than the equilibrium separation of 0.74 \AA . At their inner sides the valleys rise less steeply toward a plateau in the “northeast,” or top right-hand, corner at a level of 108.5 kcal.; this region represents complete dissociation of the system into three atoms of hydrogen.

The height of the gap at the top of the barrier through which the system has to pass before reaction can occur is at about 14 kcal. per mole, and this should be the “classical” activation energy of the process.* In the activated state, r_1 is about 1.25 \AA ,

* For 20 per cent additive energy the height of the pass is about 7 kcal. which is much closer to the experimental value, but the main features of the potential-energy surface are unchanged.

and r_2 is approximately 0.78 Å.* Since there has been little extension of the r_2 distance above the equilibrium value of 0.74 Å. the gap through which the reacting system must pass lies almost on the straight line at the bottom of the "east-west" valley, parallel to the r_1 axis. This means that a particle released from the activated position would slide down this valley with very little lateral movement. It follows, therefore, that the activation energy of the reaction must be almost entirely translational in character. A result of this nature is to be expected, for the vibrational quanta of the hydrogen molecule are about 12 to 13 kcal., and as the energy of activation is of the same order this would have to be almost completely vibrational or completely translational; the latter condition is evidently the one applicable. If the activation energy for the reaction is less than about 12 kcal., which it probably is, then it would, of course, have to be exclusively translational.

To follow the mechanics of the system when it enters the activated state, use may be made of the property of the skewed potential-energy surface which determines the amounts of vibrational and relative translational energies of the system. The principle of the method, which involves the classical equations of motion, is as follows. Suppose the kinetic energy T of the initial system to be known at any point; then, by means of Eq. (11), it may be expressed as a function of the rectangular coordinates, *i.e.*, in terms of \dot{x} and \dot{y} . Further, since the potential-energy surface has been determined, the potential energy V , at the same point, is also known in terms of x and y ; the sum of T and V then gives the Hamiltonian H of the system (see page 40) in terms of x and y , and of their derivatives with respect to time \dot{x} and \dot{y} . The generalized equations of motion are

$$\dot{p} = -\frac{\partial H}{\partial q} \quad (13)$$

and

$$\dot{q} = \frac{\partial H}{\partial p}, \quad (14)$$

* These distances give the dimensions of the activated complex in its equilibrium state; the constituent atoms presumably vibrate about the equilibrium position as in a normal molecule.

where p is the momentum and q the coordinate of a particle; in the present case the latter can be x or y , and the corresponding momenta are p_x and p_y , parallel to the x - and y -axes, respectively. It should thus be possible, from the known expression for H in terms of x , y , \dot{x} and \dot{y} , to evaluate \dot{p}_x and \dot{p}_y by differentiation with respect to x and y , respectively [Eq. (13)]. The initial values of p_x and p_y are known from the mass of the system and the details of the motion at the commencement, and hence the new values $p_x + \dot{p}_x \delta t$ and $p_y + \dot{p}_y \delta t$, after the lapse of a given time interval δt , may be calculated. The values of p_x and p_y so obtained may be employed to determine \dot{x} and \dot{y} , by means of the two forms of Eq. (14). Since the original coordinates x and y are known, the position of the system after the lapse of a time interval δt , *i.e.*, $x + \dot{x} \delta t$ and $y + \dot{y} \delta t$, can be found. The coordinates of the point and the new values of p_x and p_y are now known, and so the calculation can be repeated and the position found at the end of another small time interval, and so on. By continuing this procedure many times, the path of the particle representing the reacting system may be traced out completely from one valley to the other.

The actual computations are tedious and have been carried out only in the one case of the reaction under discussion, and even then not completely.¹⁰ The results for the $\text{H} + \text{H}_2 = \text{H}_2 + \text{H}$ reaction are shown in Fig. 28 which represents an enlarged portion of the "southwest" (lower left) corner of Fig. 27; the path of a system having 300 cal. more translational energy than is required for reaction is indicated by a series of arrows. Although the system has sufficient energy to permit it to go over the top of the pass into the shallow basin and then out of the gap on the other side, this does not take place at once. The particle representing the system is reflected back and forth at the sides of the basin, which means that there is a continual conversion of translational into vibrational energy, and vice versa. As a result, the system will wander about the potential basin for some time, and eventually either it will pass through the gap into the "north-south" valley, which means that reaction has occurred, or it will return to the valley whence it came. In the example shown in Fig. 28, the calculations have not been carried far

¹⁰ Hirschfelder, Eyring and Topley, Ref. 5; for further details, see Hirschfelder, Ref. 7.

enough to indicate which of the alternatives will occur in this instance; but the problem is theoretically soluble by classical methods, and it is probable that, if a quantum-mechanical treatment could be used, it would lead to a similar result.* For practical purposes, however, it is of interest to consider the problem statistically and to determine the number of particles entering the energy basin at various angles that go out of the two gaps. The proportions will depend upon the relative heights and cross sections of those gaps: more particles will pass out of a wide gap of low energy than would be the case if the gap

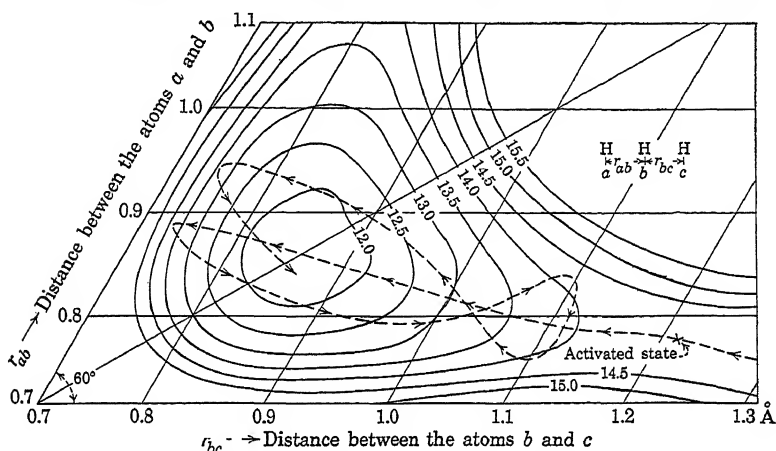


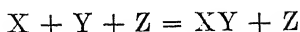
FIG. 28.—Path of H—H—H system in the basin at the top of the potential-energy barrier. (Hirschfelder, Eyring and Topley.)

were narrow and in a position of high energy. In the case of the process $\text{H} + \text{H}_2 = \text{H}_2 + \text{H}$, the two gaps must be on the same level of energy, so that half the systems reaching the activated state may be expected to undergo reaction. It is not impossible, however, that the potential basin at the top of the energy pass is a consequence of approximations and assumptions (see page 91) made in the evaluation of the energy surface, and that the true

* The principle of the quantum-mechanical treatment, which is difficult to carry out, is to consider the particle representing the system as a wave going into a medium of varying refractive index. The latter is proportional to $1/u$, where u is the velocity of the wave in the medium, and hence to p/E (see p. 29), which is equal to $[2m(E - V)/E]^{\frac{1}{2}}$, where E is the total and V the potential energy. Reflection would be indicated by the refractive index becoming imaginary; i.e., $V > E$.

surface is such that the activated state lies at the top of the pass from which it is possible to look down directly into both valleys.

Reactions Involving Three Particles.¹¹—The simplest reaction of the type



is the one involving hydrogen atoms only; the configuration of lowest potential energy, as explained above, is that in which the three atoms fall on one straight line, and information concerning the reaction may be obtained from the potential-energy surface in Fig. 27. It will be observed that when the energy of the system of three hydrogen atoms is relatively high, *e.g.*, greater than about 45 kcal., there are two areas, one on each side of the median line, in which the contours are almost parallel to the axes of the diagram.* This means that in these regions the energy may be expressed as the sum of the two independent potential terms, each being a function of a single coordinate. It is then possible to consider the transfer of energy between two degrees of freedom, *viz.*, relative translational and vibrational, associated with the two distances r_1 and r_2 ; these fix the relative translation of the linear molecule consisting of three atoms. When the potential energy on a particular surface can be expressed as the sum of two terms, each depending on a single coordinate, the surface is said to be developable in terms of those coordinates.† At the right of the median line, the surface may be regarded as developable in terms of the coordinate x_1 , which determines the translational energy, and y_1 , which gives the vibrational energy; to the left, it is developable in terms of x_2 and y_2 , the latter being chosen perpendicular to the r_2 -axis. There is no transfer of energy between the coordinates x_1 and y_1 and between x_2 and y_2 ; but when the system crosses the median line, there is a redistribution from the one set of coordinates to the other. It is readily seen from Fig. 27 that, starting from the right-hand side, if the system of three hydrogen atoms with energy greater than 45 kcal. has relative translational energy only, *i.e.*, is moving parallel to the r_1 -axis, there will be no transfer

¹¹ Eyring, Gershinowitz and Sun, Ref. 8.

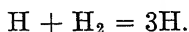
* Surfaces of this type are called "ruled surfaces."

† These are a good approximation to the "normal" coordinates of the system.

into vibrational motion until it reaches the condition when $r_1 = r_2$; the translational energy will then suddenly be redistributed among the vibrational and translational degrees of freedom in the left-hand part of the potential-energy surface. The same general arguments apply to any type of motion on the developable surface.

Suppose that the system is initially at the right-hand end of the "east-west" valley, *i.e.*, consists of $H + H_2$, and that its total energy is sufficient to permit it to dissociate into three atoms. This dissociation energy is the sum of the normal heat of dissociation, *i.e.*, 102.3 kcal. per mole, the zero-point energy, *i.e.*, 6.2 kcal. per mole, and the rotational energy. If it is postulated that the system is to remain in the original valley, the energy must be distributed in the x_1 and y_1 directions in such a way that the part along the y_1 coordinate is less than the dissociation energy. Since the surface is developable in this region, there can be no transfer of energy between the x_1 - and y_1 -directions, and so the system cannot dissociate before it reaches the median line. When it does reach this line, however, it will pass into the other valley, where the coordinates are x_2 and y_2 . It will be seen from Fig. 27 that, provided that the energy exceeds about 45 kcal., there is no pass to surmount between the valleys, and hence the activation energy is zero. As soon as the system passes the median line, the energy will be developable in terms of x_2 and y_2 ; *i.e.*, there is a redistribution of energy between the translational and vibrational degrees of freedom, and there is a definite probability that enough energy will be transferred to the y_2 -direction to make the system dissociate, *i.e.*, pass on to the plateau in the "northeast" corner which represents $H + H + H$.*

By the principle of microscopic reversibility, this will also give the probability that a system of three atoms will react to give a molecule and an atom. The mechanism of the process is the reverse of that already considered for the process



* It may be mentioned that the system must pass over a small ridge at the edge of the plateau, owing to the presence of the rotational energy; this, as will be seen later, provides the energy barrier at the top of which is the activated state (p. 127).

Of the initial energy of the system of three hydrogen atoms an appropriate amount must be in the y_2 -direction, *i.e.*, vibrational energy, and when the system crosses the median line, this is transferred into translational energy in the x_1 -direction, which is not convertible into vibrational energy. It may be noted that on account of the symmetry of the potential-energy surface the reaction can take place equally well if a certain amount of the initial energy is in the y_1 -direction; the 3H system passes first into the "east-west" valley, then crosses the median line and emerges as $\text{H} + \text{H}_2$ along the other valley.

If the third particle in the system is not a hydrogen atom, but another, *e.g.*, helium, as $\text{H} + \text{H} + \text{He} = \text{H}_2 + \text{He}$, it would be necessary to have a new potential-energy diagram.¹² In this instance, it is found from Eqs. (9) and (10) that the angle between r_1 and r_2 coordinates should be $50^\circ 46'$ and the reduction factor c is 0.79. Since a normal helium atom cannot form a valence bond with a hydrogen atom, the "east-west" valley of Fig. 27 disappears; instead, there is a high plateau with a shallow valley due to the van der Waals attractive forces that occur at relatively large values of r_2 , *viz.*, about 3.8 \AA. , and as r_2 is decreased the surface drops rapidly.* From the nature of the new surface, which is similar to that shown in Fig. 26, it is apparent that helium, or in fact any other inert molecule, cannot be anything like so efficient as a hydrogen atom in carrying away the excess energy in a linear collision. Much of the region contributing to the reaction of three hydrogen atoms, *i.e.*, the "east-west" valley, is here shut off by the high plateau; the transfer of vibrational energy, along y_2 , to translational energy, along x_1 , which is an essential factor in the stabilization of the system $\text{H}_2 + \text{H}$ formed from 3H , is now much less probable. If the system $2\text{H} + \text{He}$ has sufficient translational energy in the direction x_1 , it is possible for transfer to vibrational energy along y_2 to occur, and $\text{H}_2 + \text{He}$ will be formed, as explained on page 107.

Hydrogen as Energy Remover.—It appears, therefore, that the reason why atomic hydrogen is effective for the purpose of carrying off the excess energy of the reaction $2\text{H} = \text{H}_2$ is because of the ability of the additional atom to form a chemical bond

¹² Gershinowitz, Ref. 8.

* The van der Waals forces exist, of course, in the case of the system of three hydrogen atoms, but the attraction is unimportant compared with that due to valence forces, and so can be ignored.

with the reacting atoms.¹³ It is possible that the similar property of acting as a means for the transfer of energy (*cf.* page 290), exhibited by molecular hydrogen in many cases, is to be attributed to an analogous cause. The suggestion has been made that hydrogen molecules are much more efficient than others for the transfer of energy because of their small moment of inertia, so that a large amount of vibrational energy can be transferred to rotational energy in a single quantum.* From the discussion given above and on page 294, it is probable, however, that the ability of any molecule to transfer energy is connected with its tendency to form a complex with one or other of the reacting substances.

Nonlinear Configuration of Three Hydrogen Atoms.¹⁴—The treatment already given of the reaction $\text{H} + \text{H} + \text{H} = \text{H}_2 + \text{H}$ involves the assumption that the mechanism of the process consists in a hydrogen atom 1 approaching an unstable configuration of atoms 2 and 3, with the result that 1 and 2 form a stable molecule and atom 3 departs. This covers the cases in which the atoms are moving in a straight line or at such small angles as are included by the transverse vibrations of the activated state (*cf.* page 120). If the amplitude of these vibrations is very large, *i.e.*, for atoms approaching at very sharp angles, it is no longer permissible to assume that the surface is developable in terms of two coordinates. In these circumstances, there may be another region of the potential-energy surface that is effective for the reaction, and this would imply an additional mechanism for the process. Such a situation actually arises for the configuration in which one of the hydrogen atoms is in a direction perpendicular to the line joining the other two. The pair moving along the line react, and the third carries off the excess energy.

VIBRATION FREQUENCIES OF ACTIVATED STATE

Normal Vibration Frequencies.¹⁵—It has been seen from the treatment on pages 91 to 93 that the potential-energy surface

¹³ Eyring, Gershinowitz and Sun, Ref. 8.

* The quantum of rotational energy, for a diatomic molecule, is inversely proportional to its moment of inertia. In general, the smaller the moments of inertia of any molecule, the larger the rotational quanta.

¹⁴ Eyring, Gershinowitz and Sun, Ref. 8.

¹⁵ See E. T. Whittaker, "Analytical Dynamics," 3d. ed., Chap. VII, Cambridge University Press, 1927.

gives the energy of the activated state and the interatomic distances of a linear system of three atoms in this state. It can also be utilized to determine the normal vibration frequencies of the activated complex. These quantities are important for the evaluation of zero-point energies and for other purposes necessary for the theoretical derivation of reaction rates, as will be seen in Chaps. IV and V. The method used is based on what is known as the "theory of small vibrations" which applies to stationary points on a potential surface, *i.e.*, to maxima or minima, where the system is at equilibrium and a small change in the coordinates produces no change in the potential energy. The general expression for the potential energy V of any system for displacements q_i and q_j in the coordinates i and j is given by

$$V = V_0 + \sum_i \frac{\partial V}{\partial q_i} q_i + \frac{1}{2} \sum_{ij} \frac{\partial^2 V}{\partial q_i \partial q_j} q_i q_j + \cdots, \quad (15)$$

and at equilibrium the second term on the right-hand side is zero, since $\partial V / \partial q_i$ is zero. Neglecting third- and higher order terms, which are likely to be small for vibrations that are small compared with interatomic distances, Eq. (15) reduces to

$$V = V_0 + \frac{1}{2} \sum_{ij} \frac{\partial^2 V}{\partial q_i \partial q_j} q_i q_j. \quad (16)$$

If the activated state is chosen as the origin of the coordinates and the potential energy V_0 at this point is taken as the reference zero, then Eq. (16) can be written in the form

$$V = \sum_{ij} b_{ij} q_i q_j, \quad (17)$$

$$T = \sum_{ij} a_{ij} \dot{q}_i \dot{q}_j, \quad (18)$$

where a_{ij} is related to the masses and coordinates of the particles constituting the activated complex. Subtraction of Eq. (17)

from (18) gives

$$L = T - V = \sum_{i,j} a_{ij} \dot{q}_i \dot{q}_j - \sum_{i,j} b_{ij} q_i q_j, \quad (19)$$

where L is the Lagrangian, or kinetic potential, of the system. Differentiating Eq. (19) with respect to \dot{q}_1 and q_1 , respectively, gives

$$\frac{\partial L}{\partial \dot{q}_1} = a_{1j} \dot{q}_j \quad (20)$$

and

$$\frac{\partial L}{\partial q_1} = - \sum_j b_{1j} q_j; \quad (21)$$

and if Eq. (20) is differentiated with respect to the time t , it is seen that

$$\frac{\partial}{\partial t} \cdot \frac{\partial L}{\partial \dot{q}_1} = \sum_j a_{1j} \ddot{q}_j, \quad (22)$$

where \ddot{q}_j is the second differential with respect to the time. It follows, therefore, from Lagrange's equation of motion, *viz.*,

$$\frac{\partial}{\partial t} \cdot \frac{\partial L}{\partial \dot{q}_r} - \frac{\partial L}{\partial q_r} = 0, \quad (23)$$

that Eqs. (21) and (22) give

$$\sum_j (a_{1j} \ddot{q}_j + b_{1j} q_j) = 0. \quad (24)$$

By differentiating Eq. (19) with respect to q_2 and \dot{q}_2 , respectively, it follows in exactly the same way that

$$\sum_j (a_{2j} \ddot{q}_j + b_{2j} q_j) = 0, \quad (25)$$

and altogether there are n linear equations of this type with i varying from 1 to n , where n is the number of vibrational modes of the system in the activated state. Since the motion under consideration is periodic, *i.e.*, vibrational, the solution of these equations will be of the form

$$q_j = A_j e^{2\pi i \nu t} = A_j e^{i \lambda t},^* \quad (26)$$

* In this equation, i is used in the conventional manner for $\sqrt{-1}$.

λ being written for brevity in place of $2\pi\nu$, where ν is the frequency of the motion. If this is substituted in Eq. (24) and the similar equations, there will be obtained n equations of the type

$$\sum_{j=1}^n (-a_{ij}A_j\lambda^2 e^{i\lambda t} + b_{ij}A_j e^{i\lambda t}) = 0, \quad (27)$$

i.e.,

$$\sum_{j=1}^n (b_{ij} - a_{ij}\lambda^2)A_j = 0.$$

This gives a set of n linear equations in the A 's; and if they are to have nontrivial solutions, it follows that

$$\begin{array}{cc} b_{11} - a_{11}\lambda^2 & b_{12} - a_{12}\lambda^2 & b_{1n} - a_{1n}\lambda^2 \\ b_{21} - a_{21}\lambda^2 & b_{22} - a_{22}\lambda^2 & b_{2n} - a_{2n}\lambda^2 \\ & & = 0, \end{array}$$

$$b_{n1} - a_{n1}\lambda^2 \quad b_{n2} - a_{n2}\lambda^2 \quad b_{nn} - a_{nn}\lambda^2$$

which is an equation of the n th degree, giving n values for λ^2 . If n is 3 or more, a direct solution of Eq. (29) is not possible unless there are certain simplifying conditions that sometimes arise on account of symmetry. An indirect solution may be achieved by taking a series of values for λ^2 and evaluating the determinant D in each case; the values of D are then plotted as ordinates against the λ^2 's as abscissae, and the n values found for which the resulting curve crosses the λ^2 -axis, *i.e.*, for which $D = 0$ as required by Eq. (29). If the n solutions for λ^2 are known, the corresponding vibration frequencies can then be readily calculated, since λ is equal to $2\pi\nu$; the vibration frequency is thus given by

$$\nu = \frac{\lambda}{2\pi} \quad (30)$$

In order to solve Eq. (29), it is necessary to know the a 's and b 's for the given system. For a linear system of three atoms, such as has been the basis of most of the previous treatment of the activated state, the internal kinetic energy can

be divided into two independent parts: the first part (T_i) is due to the linear modes of vibration, and the other (T_ϕ) to the doubly degenerate bending vibration. The value of T_i is given by Eq. (4), and since Eq. (29) reduces in this case to a quadratic, the normal coordinates are obtained directly. The values of a_{11} , a_{12} and a_{22} are thus seen to be the coefficients of r_1^2 , r_{12}^2 and r_2^2 , respectively; i.e.,

$$a_{11} = \frac{m_1(m_2 + m_3)}{2M}, \quad (31a)$$

$$a_{12} = \frac{m_1 m_3}{M}, \quad (31b)$$

$$a_{22} = \frac{m_3(m_1 + m_2)}{2M}. \quad (31c)$$

The kinetic energy of the bending vibration is

$$T_\phi = \frac{r_1 r_2}{2I} \cdot \frac{m_1 m_2 m_3}{M} \phi^2, \quad (32)$$

where ϕ is the bending angle between r_1 and r_2 and I is the moment of inertia of the linear molecule; thus,

$$I = \frac{1}{M} [m_1(m_2 + m_3)r_1^2 + 2m_1 m_3 r_1 r_2 + m_3(m_1 + m_2)r_2^2]. \quad (33)$$

The quantities r_1 , r_2 , m_1 , m_2 , m_3 and M have the same significance as before (page 101). The appropriate value of a_{ij} for the determination of the frequency of the bending vibration is the coefficient of ϕ^2 in Eq. (32).

System of Three Atoms.¹⁶—If the potential-energy surface has been plotted in some detail, it is possible to derive the b_{ij} 's directly. Consider, for example, the system of three hydrogen atoms to which Fig. 27 is applicable. For 14 per cent additive (coulombic) energy the coordinates of the activated state are $r_1 = 1.25 \text{ \AA.}$ and $r_2 = 0.78 \text{ \AA.}$; and so in the neighborhood of this point the potential energy V , due to linear motion, with reference to the activated state as zero, may be represented to a first approximation by

$$V = \frac{1}{2}f_{11}(r_1 - 1.25)^2 + f_{12}(r_1 - 1.25)(r_2 - 0.78) + \frac{1}{2}f_{22}(r_2 - 0.78)^2, \quad (34)$$

¹⁶ Hirschfelder, Eyring and Topley, Ref. 5; L. Farkas and E. Wigner, *Trans. Faraday Soc.*, **32**, 708 (1936).

where f_{11} , f_{12} and f_{22} are the force constants, which are related to the b_{ij} 's, and the quantities in the parentheses are the respective displacements from the equilibrium position. The three unknowns f_{11} , f_{12} and f_{22} , which are required, may be evaluated from the potential-energy surface by taking the energies at three points, having different coordinates r_1 and r_2 , and solving the simultaneous equations. From the appropriate values of b_{11} ($= \frac{1}{2}f_{11}$), b_{12} ($= f_{12}$) and b_{22} ($= \frac{1}{2}f_{22}$), together with those of a_{11} , c_{12} and a_{22} , it is possible to derive two values of λ^2 from Eq. (29), which give the frequencies ν_s and ν_l of the two linear vibrations

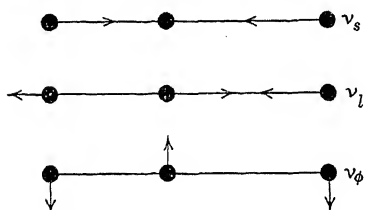


FIG. 29.—Vibrational modes of a linear triatomic system.

(Fig. 29). It is found that one of the frequencies, identified with ν_l , has an imaginary value; this means that the force constant along the corresponding normal coordinate is negative. For this type of motion, therefore, the system is in unstable equilibrium.

The bending frequency ν_ϕ is doubly degenerate, because the molecule can bend in two perpendicular planes with the same frequency. The potential energy V_ϕ for this vibration is given by

$$V_\phi = \frac{1}{2}f_\phi\phi^2, \quad (35)$$

where f_ϕ is the force constant and $\frac{1}{2}f_\phi$ is the corresponding b term. By finding from the potential-energy surface the change in the potential energy corresponding to definite values of the bending angle ϕ , it is possible to calculate the force constant from Eq. (35). To determine the a_{ij} term from Eq. (32) the moment of inertia of the activated complex is calculated from its known dimensions. The bending frequencies can now be evaluated in the usual manner, although in this instance Eq. (29) reduces to one of the first order. The results show that the linear triatomic activated complex has three vibrational modes in which it is stable, and one (ν_l) in which it is unstable. Examination of the potential-energy surface leads to the same conclusion. It is seen that any displacement of the coordinates of the activated state in any direction except that of decomposition results in an increase of potential energy; in all these directions, therefore, the activated complex behaves as a stable molecule. In

the direction of the decomposition coordinate, however, displacement leads to a decrease of potential energy and hence to decomposition. In general, an activated complex can be considered as having one normal mode of vibration less than is possessed by a stable molecule of the same type; as will be seen in Chap. IV, this missing degree of freedom is replaced by another which is equivalent to a translational movement along the decomposition coordinate.

An equivalent procedure to that described above for obtaining the b_{ij} terms is to write the expression in Eq. (1) for the energy of a system of three interacting particles involving s -electrons in the form

$$E = \rho(a + b + c) - (1 - \rho)R, \quad (36)$$

where ρ is the coulombic fraction of the total binding energy, represented by a , b and c for the three possible pairs of atoms; thus, a is equal to $A + \alpha$, b to $B + \beta$ and c to $C + \gamma$. The term R is given by

$$R = \{\frac{1}{2}[(a - b)^2 + (b - c)^2 + (c - a)^2]\}^{\frac{1}{2}} \quad (37)$$

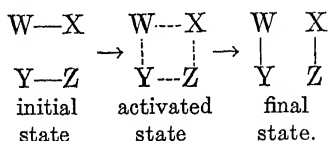
The second differentials $\partial^2 E / \partial q_i \partial q_j$, for $i = j = 1$, $i = j = 2$ and $i = 1$ and $j = 2$, which are identical with f_{11} , f_{22} and f_{12} , respectively, can then be expressed in terms of ρ , a , b , c , R and the dimensions of the activated complex; since these quantities are all known, the b_{ij} values can be determined.

FOUR-ATOM REACTIONS

Potential-energy Surface in Bond Space.¹⁷—The representation of a system of four particles requires six independent parameters (see page 90); and although the potential energies for various configurations can be calculated, their representation would require a surface in more than three dimensions and so is difficult to visualize. In order to overcome this difficulty, it is necessary to abandon the use of configuration space to represent the variation of the potential energy of the reacting system and to adopt a form of representation in "bond space"; for this purpose the potential energy is given in terms of two bond

¹⁷ Altar and Eyring, Ref. 2.

energies instead of six distances. Consider, for example, the reaction between two diatomic molecules WX and YZ; thus:



If the energies of the diatomic molecules are a_1 for WX, a_2 for YZ, b_1 for WY, b_2 for XZ, c_1 for WZ and c_2 for XY, then in the initial state, when WX and YZ are relatively far apart, $a_1 + a_2 = a$ has its maximum value, whereas b_1 , b_2 , c_1 and c_2 are almost zero; in the final state $b_1 + b_2 = b$ is a maximum, and the other binding energies are all very small. In terms of the energies of the diatomic molecules, therefore, the reaction starts with a maximum value of a and proceeds to a maximum value of b by the path requiring the least expenditure of energy; this important fact, together with the form of the analytical expression for the energy (page 76), permits the reaction path to be plotted in terms of two variables in the so-called "bond space." Different values of the bond energies a and b are taken, and the value of c , equal to $c_1 + c_2$, that together with them gives the lowest potential energy of the system is found; the corresponding values of E are then plotted against a and b , and the equipotential lines so obtained give the potential-energy surface in bond space. It can be readily seen from the arguments on page 89 (*cf.* Fig. 11) that the lowest value of E for a given a and b is obtained when c is a minimum, provided that c is the lowest of the three quantities a , b and c . The latter condition is almost invariably applicable, since c_1 and c_2 are taken as referring to the pairs of atoms that have the greatest separations (see Fig. 12). It is necessary, therefore, to find the lowest value of c , *viz.*, $c_1 + c_2$, for given values of a and b and then to calculate the corresponding energy E by means of the London equation (1).

The determination of the smallest value of c for a given a and b is greatly facilitated by means of a mechanical device consisting of six hinged or sliding scales; on each of these scales is marked the value of one of the six bond energies, *viz.*, a_1 , a_2 , b_1 , b_2 , c_1 and c_2 , as a function of the interatomic distances. The

data required for the preparation of these scales are obtained from the Morse equation for the diatomic molecules WX, YZ, WY, XZ, WZ and XY, respectively. These scales are linked together in such a way as to represent a model of a planar configuration of four atoms; as has already been shown (page 90),

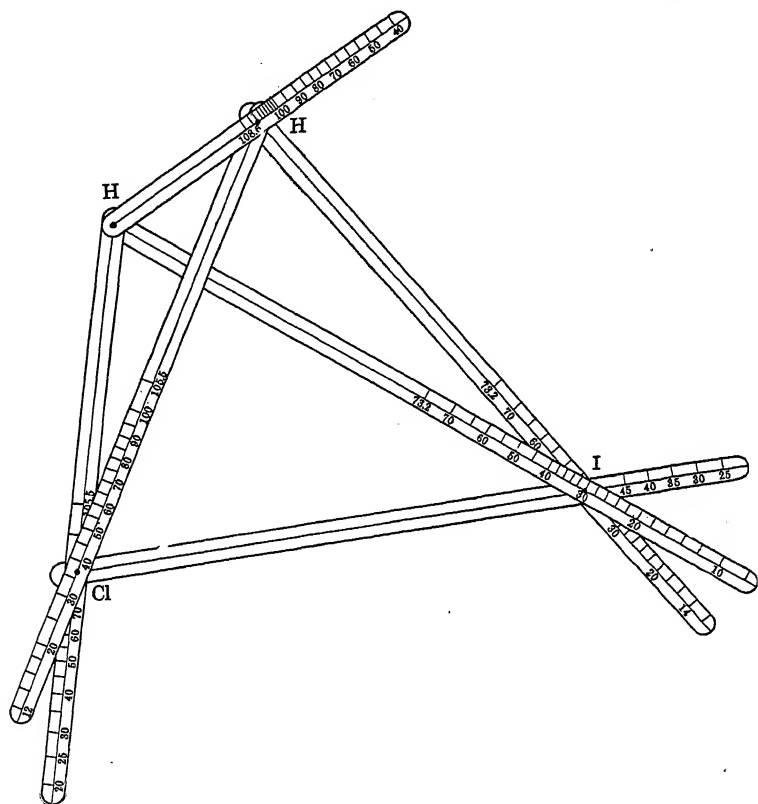


FIG. 30.—Sliding rulers for determining four-atom system of minimum energy. (Altar and Eyring.)

the potential energy of a system of four electrons is a minimum when they lie in one plane. A particular case, for the reaction $\text{H}_2 + \text{ICl} = \text{HI} + \text{HCl}$, is shown in Fig. 30. By moving the scales on their hinges or slides, varying a_1 , a_2 , b_1 and b_2 but keeping the sums $a_1 + a_2 (= a)$ and $b_1 + b_2 (= b)$ constant, it is possible to find the configuration giving the lowest value for $c_1 + c_2 (= c)$. In other words, without varying four of the six dimensions of the model, it is possible to adjust the configura-

tion so that the sum of the remaining pair of dimensions, *viz.*, the diagonals, is a minimum. The process is then repeated with different combinations of the distance corresponding to a_1 and a_2 , adding up to the same a , and of b_1 and b_2 , giving the same b , until an absolute minimum for the given values of a and b is found. The procedure is then repeated with new values of a and b until enough figures have been obtained. The potential energies for the various a 's and b 's and the appropriate c 's that

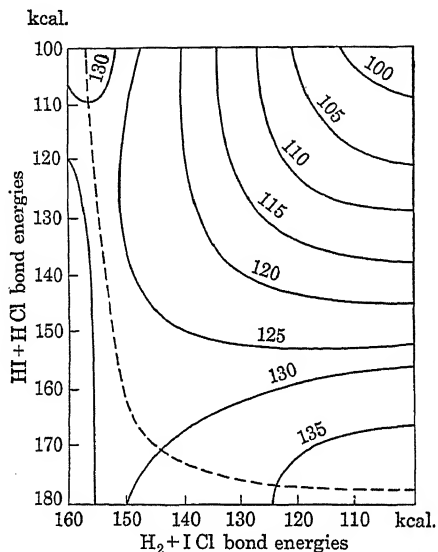


FIG. 31.—Potential-energy surface in bond space for the reaction $\text{H}_2 + \text{ICl} = \text{HI} + \text{HCl}$. (Data from Altar and Eyring.)

will make the energy a minimum are then used to calculate the actual value of E , by means either of Eq. (1) or of its equivalent geometrical construction (page 90).

The data so obtained are plotted on a series of equipotential curves as a function of the bond energies a and b , *i.e.*, of the molecules $\text{WX} + \text{YZ}$ and $\text{WY} + \text{XZ}$, respectively. The type of diagram obtained is shown in Fig. 31; it is very similar in form to the potential-energy surfaces in configuration space for three-particle systems, but the coordinates have now a different significance.* The reaction path is shown by the dotted line;

* It may be pointed out that there is no fundamental difference between potential-energy surfaces in configuration and bond spaces. In the former,

as seen on page 122, the system starts from the region where a is a maximum and goes to that in which b is a maximum, by the easiest possible path. The highest point that the system has to surmount in this path is the position of the activated state; and the potential energy at that point, with reference to the initial state, gives the activation energy of the reaction.

To determine the dimensions of the activated complex, it is necessary to know the actual values of the bond energies a_1 , a_2 , b_1 , b_2 , c_1 and c_2 that give the activation energy. The distances r_1 , r_2 , r_3 , r_4 , r_5 and r_6 corresponding to these energies can then be readily derived from the Morse curves of the six diatomic molecules; from these dimensions, it is possible to evaluate the moments of inertia of the activated complex that are required for the statistical calculation of reaction rates (Chap. IV).

Vibration Frequencies.—The activated state for a four-particle system, like that for one of three particles, is an equilibrium position, since the potential energy is a minimum in all directions except along the reaction path where it is a maximum. It is thus possible to apply the theory of small vibrations to calculate the vibration frequencies in the activated state, the b_{ij} terms being obtained by the procedure outlined on page 115. Of the six normal vibration frequencies of a nonlinear system of four atoms, five are in one plane whereas the sixth is a twisting vibration out of the plane. It is possible to treat these groups separately, so that the sixth-order determinant that has to be solved divides into a fifth-order determinant and a linear equation. The values of a_{ij} are derived in the usual manner, by writing out the kinetic energy of the system and transforming to normal coordinates; the procedure is not simple, but it has been worked out in some detail.¹⁸ The solution of the fifth-order determinant is carried out by the graphical method described on page 118; it is found that four of the frequencies are real, but one has an imaginary value, as in the case of the activated complex consisting of three atoms. The sixth normal vibration

the coordinates are the distances r_1 and r_2 ; and these are, of course, related to the energies of the bonds XY and YZ, which are a and b for a system of three atoms.

¹⁸ Altar and Eyring, Ref. 2.

frequency is given by the solution of the linear equation for the twisting motion.

Symmetrical Activated Complex.¹⁹—If the activated complex possesses a certain degree of symmetry, the calculation of the vibration frequencies can be simplified by reducing the order of the determinant. In a reaction of the type

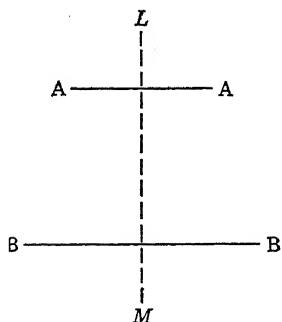
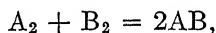


FIG. 32.—Activated complex A_2B_2 with plane of symmetry.

of which $H_2 + I_2 = 2HI$ is an example, the system has two planes of symmetry in the activated state; one of these planes is shown at LM (Fig. 32), and the other is the plane of the complex, which is normal to LM . As a result of this symmetry, the six modes of vibration can be divided into three classes. The six vibrations, which are shown in Fig. 33, can be classified into three

groups according to their behavior when subjected to symmetry operations. First, reflection in the plane of the molecule changes the sign of the bending vibration I, but leaves all the others unchanged; second, reflection in the LM plane changes the sign of the displacements in V and VI but does not affect the others. The three classes of vibration thus consist of: (a) I; (b) II, III and IV; and (c) V and VI. Since these can be treated sepa-

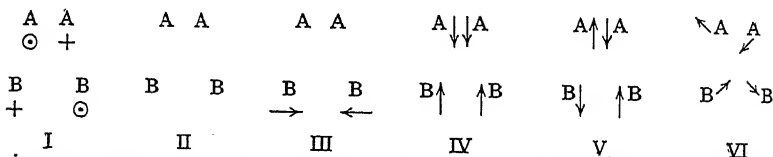


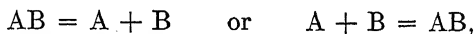
FIG. 33.—Modes of vibration of activated complex A_2B_2 . (Altar and Eyring.)

ately, the problem of the evaluation of the vibration frequencies is reduced to the solution of a third-order, a second-order and a linear equation. This is, of course, a much simpler problem than the solution of a fifth-order determinant, and hence it is advantageous to make use of the classification based on symmetry considerations.

¹⁹ A. Wheeler, B. Topley and H. Eyring, *J. Chem. Phys.*, **4**, 178 (1936).

DISSOCIATION AND ASSOCIATION REACTIONS

Rotational-energy Barriers.²⁰—Reactions involving the combination of two atoms to form a molecule, or those in which a molecule dissociates in a unimolecular manner, or, in fact, all reactions of the type



where A and B may be atoms or molecules, present a special problem in connection with the subject of potential-energy surfaces. The usual form of "surface," which is actually two-dimensional for two atoms, is the simple potential-energy curve, such as is shown in Fig. 34; this curve has no maximum, except at infinity, and so it would appear that the position of the activated state cannot be determined. It is important to bear in mind, however, that the curve gives the potential energy of a system of two atoms as a function of the distance between them only for the case in which the two atoms are approaching

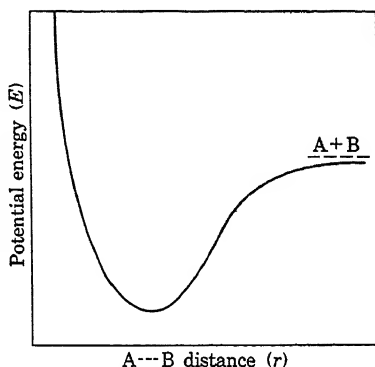


FIG. 34.—Potential-energy curve for diatomic molecule.

or receding along the same straight line. In general, this situation will not be encountered, for the atoms will have a relative angular momentum, which is equivalent to a rotation in two degrees of freedom, when they come together. The kinetic energy of rotation for each quantum state and for each interatomic distance must be added to the potential energy given by the simple curve shown in Fig. 34. The result will be that a maximum will appear as shown diagrammatically in Fig. 35; here I is the original potential-energy curve, and II shows the result of adding the rotational energy. A different curve is obtained for each value of the rotational quantum number, but the general form may be taken as being the same in all cases.

From left to right, curve II represents the change of potential energy in the dissociation $AB = A + B$; from right to left, the

²⁰ Eyring, Gershinowitz and Sun, Ref. 8.

change in the association reaction $A + B = AB$. The same activated state is, of course, applicable to both reactions; it is seen that by the inclusion of rotational energy its position has been shifted from infinity to an apparently definite position, which depends on the rotational quantum number J in the activated state. As the value of J becomes larger, the rotational energy increases and it is evident from Fig. 35 that the inter-

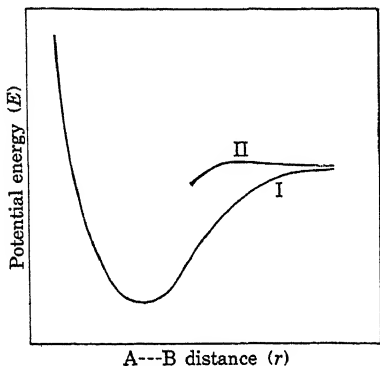


FIG. 35.—Potential-energy curve for diatomic molecule; (I) without rotational energy, (II) including rotational energy.

atomic separation in the activated state will become smaller. The actual separation for each J value may be obtained in the following manner. The total energy ϵ represented by curve II is the sum of the electronic and vibrational energies ($\epsilon_e + \epsilon_v$), as given by the Morse equation, and the rotational energy ϵ_J . As seen on page 92, the former can be expressed as a function of the interatomic distance r , and so also can the latter; for if there is no

interaction between the various forms of energy, the rotational energy is

$$\epsilon_J = J(J + 1) \frac{h^2}{8\pi^2 I}, \quad (38)$$

where I , the moment of inertia of the molecule, is equal to μr^2 , μ being the reduced mass. It is thus possible to write an equation for ϵ corresponding to each value of J with r as the only variable. Since the energy in the activated state is a maximum, it follows that $d\epsilon/dr$ must be zero; and so if the resulting expression is differentiated with respect to r and the derivative set equal to zero, the solution gives the interatomic distance r_J for the maximum in the potential-energy curve corresponding to a particular rotational quantum number J . By repeating this procedure a number of times, it is possible to calculate r_J for a series of J 's, and the results may be plotted as shown in Fig. 36, where the curves are for the reactions $2H = H_2$ or $2D = D_2$, or the

reverse reactions in each case.* It is seen, as expected, that the interatomic separation in the activated state decreases with increasing rotational quantum number.

The next matter to consider is the most probable value of J for the activated complex at any temperature, for it will then be possible, by means of Fig. 36, to find the most probable interatomic distance in the activated state; this, incidentally, is equivalent to the "collision diameter" in an association reaction. The probability of the existence of any particular rotational-

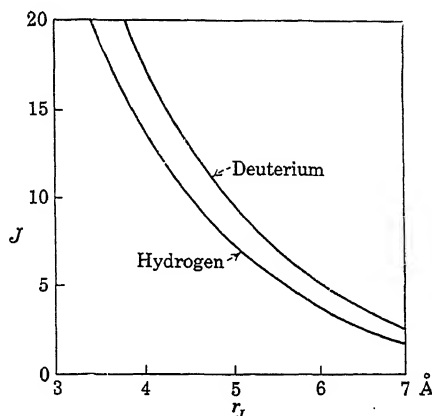


FIG. 36.—Interatomic distances in the activated state for different rotational quantum numbers. (Eyring, Gershinowitz and Sun.)

energy state is given by the quantity $(2J + 1) e^{-\epsilon_J/kT}$, where $2J + 1$ is the multiplicity of the state and ϵ_J is the rotational energy with reference to some standard state. If the latter is chosen as the energy of the dissociated atoms, then it can be seen from Fig. 37 that the probability of the activated state is $(2J + 1) e^{-\epsilon_J^*/kT}$, where

$$\epsilon_J^* = \epsilon_J - (D - \epsilon_v); \quad (39)$$

in this equation, D is the dissociation energy and ϵ_v is the vibrational energy, in excess of the zero-point value in each case. The rotational energy ϵ_J corresponding to any value of J can be obtained from Eq. (38), Fig. 36 being used to give the interatomic distance required for the calculation of I , and ϵ_v is derived from

* It will be evident that the curves have definite significance for *integral* values only of the rotational quantum number.

the potential-energy curve or the equivalent Morse equation. Hence, if D is known for a particular reaction, it is possible to calculate ϵ_J^* and thus to determine the probability of the activated state for a series of rotational quantum numbers at any particular temperature. The necessary calculations have

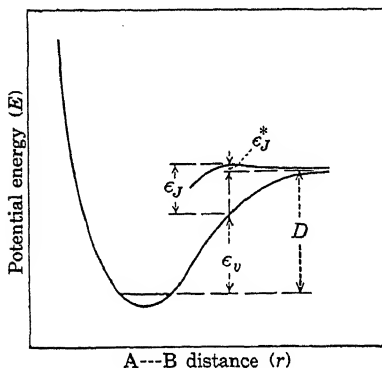


FIG. 37.—Potential-energy curve for diatomic molecule showing effective activation energy due to rotation.

been made for the reactions $2\text{H} = \text{H}_2$ and $2\text{D} = \text{D}_2$ at 500°K , and resulting plots of $(2J+1) e^{-\{\epsilon_J - (D - \epsilon_v)\}/kT}$ against J are shown in Fig. 38.† The most probable value of the rotational quantum number in the D_2 activated complex is just over 10, and by examination of Fig. 36 this is seen to correspond to an interatomic distance of about 4.9 \AA . Similarly, the most probable interatomic distance for the H_2 activated complex is 4.8 \AA . These figures give the most probable collision diameters;

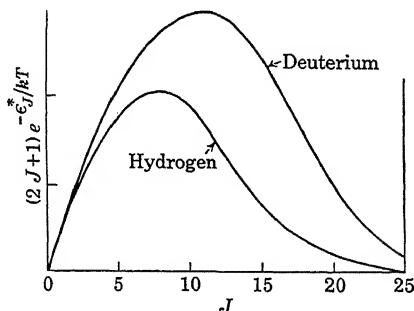


FIG. 38.—Determination of the most probable rotational quantum number in the activated state. (Eyring, Gershinowitz and Sun.)

but a more useful datum is the mean collision diameter, for it is evident from Fig. 38 that the activated state is distributed over a number of rotational levels. At appreciable temperatures the sum of the probabilities for the different rotational levels, which

† As in Fig. 36, points on the curves have physical significance only if they correspond to integral values of the rotational quantum number J .

may be taken as equal to the areas under the appropriate curves in Fig. 38, approaches a limiting value $8\pi^2 \bar{I} kT / h^2$ (cf. page 179); thus,

$$\sum_{J=0}^{\infty} (2J + 1) e^{-\epsilon_J^* / kT} = \frac{8\pi^2 \bar{I} kT}{h^2}, \quad (40)$$

where \bar{I} may be regarded as the average moment of inertia of the activated complex. It is thus possible to evaluate \bar{I} , and, putting this equal to $\mu \bar{r}_J^2$, the mean interatomic separation in the activated state (\bar{r}_J) can be evaluated; for hydrogen, this is 4.4 Å., and for deuterium 4.1 Å. In general, for the association of two particles, atoms or radicals, the apparent collision diameter, corresponding to the dimensions of the activated state, will be determined by the angular momentum; at room temperature, it will be about 4 to 5 Å.

The activation energy for an association reaction is given by the value of ϵ_J^* corresponding to the mean separation in the activated state; this is so small that it may be neglected, so that the combination of two atoms or radicals generally requires little or no activation energy. For the reverse dissociation reaction, it is evident that the activation energy may be taken as equal to the energy of dissociation D , reckoned from the lowest vibrational-energy level. This rule applies to unimolecular reactions, unless the process is accompanied by an electron transition or other reorganization within the molecule; these would result in a reduction of the activation energy.

Combination of Free Radicals.²¹—The union of two free radicals presents a special modification of the case of the combination of atoms; in this instance the separation of the centers of the approaching radicals in what may be regarded as the activated state is so large that the vibrational and rotational degrees of freedom may be assumed to be the same as in the free radicals themselves. There is probably no activation energy in the true sense of the term; the radicals attract each other at large distances chiefly on account of polarization forces, and this is opposed by the centrifugal force of the rotation of the two radicals considered as equivalent to two atoms. The superposi-

²¹ E. Gorin, *Acta Physicochim. U.R.S.S.*, **9**, 691 (1938); cf. H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936).

tion of these two forces gives rise to a slight potential barrier, the top of which corresponds to the activated complex. The distance between the centers of gravity of the radicals in this activated state may be obtained by a simple calculation of the maximum of the energy curve. The energy of attraction, due to polarization, between two radicals at relatively large distances is given by

$$E_{\text{pol.}} = \frac{1}{2} \cdot \frac{\alpha_A \alpha_B}{r^6} \frac{\mathcal{I}_A \mathcal{I}_B}{\mathcal{I}_A + \mathcal{I}_B} \quad (41)$$

where α_A and α_B are the polarizabilities and \mathcal{I}_A and \mathcal{I}_B the ionization potentials of the radicals A and B, and r is their distance apart. The centrifugal force in the opposite direction resulting from rotation, on the assumption that the combination of the two radicals behaves as a diatomic rotator, is

$$E_{\text{rot.}} = \frac{J(J+1)\hbar^2}{8\pi^2\mu r^2}, \quad (42)$$

where J is the rotational quantum number, which can have any integral value including zero, and μ is the reduced mass of the rotator. By subtracting Eq. (41) from (42), differentiating the result with respect to r , and equating to zero, so as to give the value of r^* for the maximum in the energy curve, it is found that

$$r^* = \frac{36\pi^2\mu\alpha_A\alpha_B \left(\frac{\mathcal{I}_A\mathcal{I}_B}{\mathcal{I}_A + \mathcal{I}_B} \right)^{1/4}}{J(J+1)\hbar^2} \quad (43)$$

The quantity that expresses the apparent activation energy is now found by inserting this value for r in the equations for the polarization and rotational energies and subtracting, thus:

$$E_{\text{rot.}} = E_r^{\ddagger} \quad \nu_{\text{pol.}} = \frac{[J(J+1)\hbar^2]^{3/2}}{72(\pi^2\mu)^{3/2} \left[\alpha_A\alpha_B \left(\frac{\mathcal{I}_A\mathcal{I}_B}{\mathcal{I}_A + \mathcal{I}_B} \right) \right]^{1/2}} \quad (44)$$

The application of this result will be considered more fully in Chap. V.

The foregoing treatment was first used in connection with the reaction between H_2 and H_2^+ ; here again the separation in the "activated" state is presumably large. The polarization energy

is now $\alpha\epsilon^2/2r^4$, where ϵ is the electronic charge and α is the polarizability of the hydrogen molecule; by working in exactly the same manner as described above, it follows that in the activated state

$$r^* = \left[\frac{J(J+1)\hbar^2}{8\pi^2 m_H \alpha \epsilon^2} \right]^{1/2}, \quad (45)$$

where m_H is the mass of a hydrogen atom. The corresponding activation energy is then

$$E_{\text{act.}} = E_{\text{rot.}}^* - E_{\text{pol.}}^* = \frac{J^2(J+1)^2\hbar^4}{128\pi^4 m_H^2 \alpha \epsilon^2}. \quad (46)$$

STABLE AND UNSTABLE COMPLEXES

Potential-energy Basins.—It was mentioned on page 96 that potential-energy surfaces frequently have a basin, or depression, at the top of the energy pass between the valley representing reactants and that for the resultants. It is possible that the shallow basins of this type are to be ascribed to the decrease in the proportion of coulombic energy at small internuclear separations (*cf.* page 83) where such basins appear. For the construction of the potential-energy surface the assumption is made, as described on page 96, that the fraction of coulombic energy is constant, and this may yield somewhat misleading results. It is not certain, therefore, if the depressions have any real significance; it is nevertheless of interest to consider what they may mean.

The H_3 Complex.²²—In the case of the reaction between H and H_2 , the floor of the basin is about 1.5 kcal. below the rim; this would suggest that a linear molecule H_3 , which is 1.5 kcal. more stable than the activated complex, may have some existence. It can, however, be no more than transient, because the potential energy of the H_3 molecule would be actually greater by 12 kcal. than its constituents $H + H_2$. It is evident, therefore, that the linear H_3 molecule would be metastable, and it would have to acquire energy approximately equal to the small depth of the basin, *viz.*, 1.5 kcal., before it decomposed; the life period of the metastable H_3 molecule may thus be expected to be very short. This life period, which may be regarded as a measure of the

²² Eyring, Gershinowitz and Sun, *Ref.* 8.

time of duration of a collision between H and H₂, can be calculated theoretically by utilizing the fact that the mean life is the reciprocal of the specific rate of the reaction $H_3 = H_2 + H$; this rate can be obtained by the statistical mechanical methods described in Chap. IV. For the purpose of this computation, it is necessary to know the moment of inertia and the normal vibration frequencies of the H₃ molecule and of the activated state; these quantities can be derived, by the methods already outlined, from the potential-energy surfaces. In this manner a mean life of 6.3×10^{-13} sec. has been found for the H₃ molecule, on the assumption that the coulombic energy is 14 per cent of the total binding energy; for 20 per cent additive energy the mean life is calculated to be 2.7×10^{-12} sec.²³ Comparison of these values with those calculated for the activated state in the absence of a minimum shows that the H₃ system must roll about the basin 10 to 100 times (*cf.* Fig. 28) before dissociation into H₂ and H occurs. The calculations of the mean life must, of course, be regarded as approximate in view of the general limitations of the potential-energy surface obtained by the semi-empirical method.

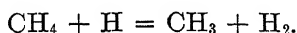
The Cl₃ Complex.²⁴—Although the H₃ molecule has a very short life, it is possible that other triatomic molecules of a similar nature, *e.g.*, Cl₃, are stable. Consideration of the potential-energy surface for the reaction $X + X_2$, where X is a halogen, shows that the X₃ molecule is from 2 to 4 kcal. stable with respect to its constituents X and X₂. In the process $Cl + Cl_2 = Cl_3$, for example, it appears that ΔH is -4.1 kcal. This figure is derived from a potential-energy surface constructed on the assumption that 10 per cent of the binding energy of the halogen molecule is additive. In view of the fact that the electrons concerned in the reaction are probably 3*p*, the coulombic energy may well be a much larger proportion of the total (*cf.* page 84); this would have the effect of making the molecule Cl₃ even more stable than is indicated above. If these conclusions are correct, then it follows that many reactions, such as photochemical processes at room temperature, in which dissociation of the chlorine has been postulated as a primary step, should involve

²³ Hirschfelder, *Ref. 7*; see also N. Rosen, *J. Chem. Phys.*, **1**, 319 (1933); G. E. Kimball, *ibid.*, **5**, 310 (1937).

²⁴ G. K. Rollefson and H. Eyring, *J. Am. Chem. Soc.*, **54**, 2661 (1932).

Cl_3 molecules. In some of the attempts to develop a mechanism for the photochemical reaction of hydrogen and chlorine, the Cl_3 molecule has been postulated as an intermediate, but it is not generally agreed that this is necessary.

The CH_5 Complex.²⁵—A case of special interest in the chemistry of the hydrocarbons arises from a consideration of the potential-energy surface for the reaction between methane and atomic hydrogen,



The surface has been calculated on the assumption that the hydrogen atom approaches the methane in the

FIG. 39.—Approach of hydrogen atom to a molecule of methane.

direction of one of the $\text{H}-\text{C}$ bonds, and the problem is treated as essentially one of three electrons, *i.e.*, one each from CH_3 , H_{α} , and H_{β} (Fig. 39). The additional resonance energy resulting from the complete nine-electron problem makes very little difference to the final conclusions. The result of the computation is shown

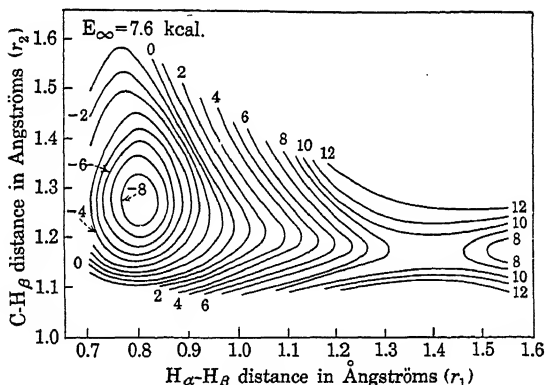


FIG. 40.—Potential-energy surface for the system of a hydrogen atom and a molecule of methane. (Gorin, Kauzmann, Walter and Eyring.)

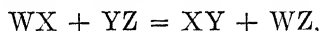
in Fig. 40, the energy of the system $\text{CH}_4 + \text{H}$ being taken as zero. The interesting aspect of this diagram, for present purposes, is the relatively deep basin appearing at the top of the energy pass. Since the bottom is 8 kcal. below the level of $\text{CH}_4 + \text{H}$, it appears possible that a stable molecule, which may

²⁵ Gorin, Ref. 21; E. Gorin, W. Kauzmann, J. Walter and H. Eyring, *J. Chem. Phys.*, **7**, 633 (1939).

be formulated as H—H—CH_3 , may exist. The decomposition of this substance into CH_4 and H would require an activation energy of approximately 17 kcal., for this is the distance from the bottom of the depression representing the CH_5 complex to the top of the rim over which it would have to pass before entering the valley parallel to the $\text{H}_\alpha\text{—H}_\beta$ -axis.* The relative stability of the H—H—CH_3 molecule would account for some interesting phenomena in reactions involving methane and hydrogen (see page 257).

RESONANCE (EXCHANGE) ENERGY

Crossing of Potential-energy Surfaces.²⁶—In the reaction



the bond assignments in the initial and final states are represented by A and B, respectively, thus,



and since a third state, involving crossed bonds (*cf.* page 60), which is a combination of A and B is possible, the energy of the system is given by the solution of the secular equation (173) of Chap. II. It is from this equation that Eq. (206), which gives the complete potential-energy surface, is derived. Hence, one solution of the equation

$$\begin{array}{cc} H_{AA} - \Delta_{AA}E & H_{AB} - \Delta_{AB}E \\ H_{BA} - \Delta_{BA}E & H_{BB} - \Delta_{BB}E \end{array} = 0 \quad (47)$$

may be regarded as representing the potential-energy surface for the reaction under consideration. It will be recalled (page 68) that the quantities H and Δ are defined by

$$H_{AA} = \int \Psi_A \mathbf{H} \Psi_A d\tau, \quad H_{BB} = \int \Psi_B \mathbf{H} \Psi_B d\tau, \\ H_{AB} = H_{BA} = \int \Psi_A \mathbf{H} \Psi_B d\tau, \quad (48)$$

* It is possible, from the shape of the potential-energy surface in Fig. 40, that decomposition of CH_5 into $\text{CH}_3 + \text{H}_2$, *i.e.*, passage along the valley parallel to the C—H_β -axis, might require a smaller activation energy; the value would, however, be at least 6 to 8 kcal.

²⁶ R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, **31**, 604, 1375 (1935); M. G. Evans and M. Polanyi, *ibid.*, **34**, 11 (1938); M. G. Evans and E. Warhurst, *ibid.*, **34**, 614 (1938); **35**, 593 (1939).

$$\Delta_{AA} = \int \Psi_A \Psi_A d\tau, \quad \Delta_{BB} = \int \Psi_B \Psi_B d\tau, \\ \Delta_{AB} = \Delta_{BA} = \int \Psi_A \Psi_B d\tau, \quad (49)$$

where the Ψ 's are the eigenfunctions for the states A and B. If there is no interaction between the two states or, as is frequently stated, if the eigenfunctions A and B do not overlap, the terms H_{AB} and Δ_{AB} are zero; the solutions of Eq. (47) are then

$$(a) E_A = H_A \quad \text{and} \quad (b) E_B = \frac{H_B}{\Delta_{BB}} \quad (50)$$

Equation (50a) gives the potential-energy surface of the system having the bond assignments of the initial state, and (50b) gives the corresponding surface for the bond assignments of the final state.* The two surfaces defined in this manner intersect along a line for which E_A is equal to E_B ; and the lowest point on this line represents the energy of activation for the reaction in which the configuration A passes into B. If the configurations of the initial and final states overlap

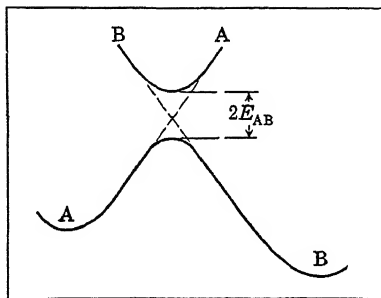


FIG. 41.—Crossing of potential-energy surfaces.

to any appreciable extent, it is necessary to include the exchange integrals H_{AB} and Δ_{AB} ; as a result there will be a rounding off of the surfaces along the line where they cross. This is seen diagrammatically in Fig. 41, which shows a profile of the potential-energy surfaces A and B and the rounding off at the crossing point that results from the interaction of the eigenfunctions for the states A and B. The consequent decrease in activation energy, E_{AB} , is equal to the resonance, or exchange, energy in the activated state. It arises because at the crossing point the system is degenerate; there are two eigenfunctions Ψ_A and Ψ_B for the two different ways of assigning the bonds, but the energy is the same

* The same conclusion may be reached by considering two independent states A and B; for each the wave equation is of the form $\mathbf{H}\psi_i = E\psi_i$. Upon multiplying both sides by ψ_i and integrating over the configuration space, it is seen that $\int \psi_i \mathbf{H} \psi_i d\tau = E \int \psi_i \psi_i d\tau$, which is the same as $E = H_{ii}/\Delta_{ii}$.

where the surfaces cross. Application of perturbation theory or the variation theorem then leads to two values for the energy, viz., $E_A + E_{AB}$ (upper) and $E_A - E_{AB}$ (lower), where E_A and E_B are now, of course, equal. There is consequently a splitting into an upper and a lower surface, as indicated in Fig. 41, corresponding to the two solutions of Eq. (205), Chap. II; the lower surface contains the actual reaction path.

Magnitude of the Resonance Energy.—It was seen on page 75 that the quantity Δ_{AA} in Eq. (50) is approximately equal to the coefficient of Q , the coulombic energy, in H_{AA} ; and according to Eq. (197), Chap. II, the latter, and hence in this case E_A , is given by

$$E_A = \frac{H_{AA}}{\Delta_{AA}} = Q + [(ab) + (cd)] - \frac{1}{2}[(ac) + (bd) + (ad) + (bc)] \quad (51)$$

$$= Q + J_b - \frac{1}{2}J_n, \quad (52)$$

where J_b is the sum of the exchange integrals for the bonded

atoms and J_n is the corresponding sum for the nonbonded atoms. Upon writing, as on pages 75 and 76, $\alpha_1 + \alpha_2 = \alpha$ for $(ab) + (cd)$, $\beta_1 + \beta_2 = \beta$ for $(ac) + (bd)$ and $\gamma_1 + \gamma_2 = \gamma$ for $(ad) + (bc)$, it follows that

$$E_A = Q + [\alpha - \frac{1}{2}(\beta + \gamma)]. \quad (53)$$

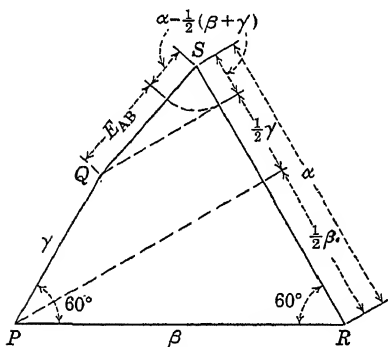


FIG. 42.—Graphical determination of resonance energy in the activated state.

If the resonance energy is included, then the energy of the upper surface is given by Eq. (205) Chap. II, thus,

$$E = Q + \left\{ \frac{1}{2}[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2] \right\}^{1/2}; \quad (54)$$

and hence the value of the resonance energy is

$$E_{AB} = E - E_A = \left\{ \frac{1}{2}[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2] \right\}^{1/2} - [\alpha - \frac{1}{2}(\beta + \gamma)]. \quad (55)$$

The magnitude of this energy can be readily derived from a simple geometrical construction, similar to that described on page 89 for determining the first term on the right-hand side of Eq. (55).

The quantity $\alpha - \frac{1}{2}(\beta + \gamma)$ is obtained by drawing perpendiculars from P and Q on to RS , as shown in Fig. 42. The determination of the resonance energy by the construction shown is evident. It is clear that, since the exchange energies α , β and γ constitute a large proportion of the total binding energy, the resonance energy may well be quite considerable. It is only in special cases, *e.g.*, if both β and γ are relatively small compared with α , or for a non-adiabatic process (*cf.* page 149), that the resonance energy is negligible.

POTENTIAL-ENERGY PROFILES

Sections of Potential-energy Surface.²⁷—A useful method of representing the path of a chemical reaction of the type

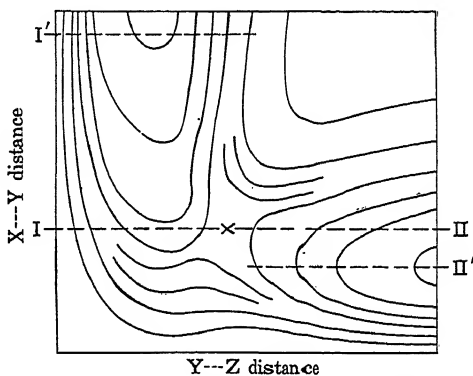


FIG. 43.—Sections through a potential-energy surface.

$X + YZ = XY + Z$, where X , Y and Z are either atoms or radicals (*e.g.*, CH_3) which do not change in the reaction, is the following; it brings to light the nature of some of the factors determining the activation energy. Suppose Fig. 43 represents the potential-energy surface for the reaction under consideration; a section at I' shows the variation of potential energy of the molecule YZ as a function of the distance $Y-Z$ when X is far away. The lowest part of the curve, which is of the familiar form for a diatomic molecule, is shown at I' in Fig. 44 where the ordinates are the energy and the abscissae the $Y-Z$ distances; this may be regarded as the potential-energy curve of the initial state of the reaction. As X is brought closer to YZ , the potential-energy curves are given by a series of sections of Fig. 43 parallel

²⁷ Ogg and Polanyi, Ref. 26; Evans and Polanyi, Ref. 26.

to I' ; finally, when X is close enough for the activated state $X-Y-Z$ to be formed, the section would be at I . The shape of the resulting curve, on the assumption there is no reaction, would be of the form of I in Fig. 44; and if X does not interact appreciably with Z , this is similar to that of the potential-energy curve I' for the normal YZ molecule. The increase in energy from the lowest portion of I' to that of I is due to the repulsion energy between X and YZ in going from the initial to the activated state.

Consider next a section at II' , through the bottom of the "east-west" valley of Fig. 43; in going from right to left, *i.e.*, as

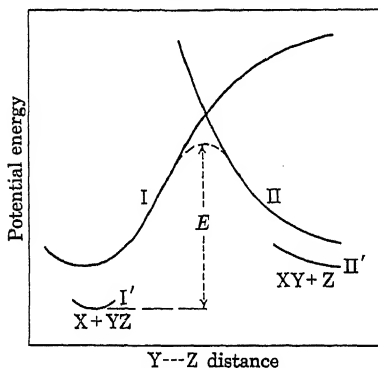


Fig. 44.—Potential-energy curves for the reaction $X + YZ = XY + Z$. (Ogg and Polanyi; Hinshelwood, Laidler and Timm.)

as Z is brought up closer to XY in which the atoms retain their equilibrium separation, the potential energy rises on account of the repulsion between XY and Z . The corresponding "repulsion curve," as it is frequently called, for various $Y-Z$ distances is shown, in part, at II' on Fig. 44. Different curves, similar in shape but at higher levels, are obtained if the $X-Y$ separation is increased. For the dimensions corresponding to the activated state the repulsion curve, provided that no reaction occurred, would be given by the section through the potential-energy surface at II ; this curve is shown at II in Fig. 44. The difference between the lowest portions of II and II' is equal to the energy required to stretch the $X-Y$ bond from its equilibrium distance to that in the activated state, provided that the atom Z is far away, *i.e.*, when the $Y-Z$ distance is large.

As stated above, the separate curves I and II imply that there is no reaction of $X + YZ$ to form $XY + Z$, or the reverse; but the crossing of the curves shows that reaction does actually take place. If there were no overlapping of the eigenfunctions of initial and final states, *i.e.*, if the resonance energy were zero, the intersection of the curves I and II would give the activation point for the reaction, since at this point both the distances

$X-Y$ and $Y-Z$ are those for the activated state. The inclusion of resonance energy results in a rounding off, as shown by the dotted line in Fig. 44, so that there is a continuous energy transition from $X + YZ$ to $XY + Z$. The maximum of the actual curve represents the activated state; and the activation energy E , disregarding zero-point energies, is equal to the vertical distance from this maximum to the bottom of I' , which represents the initial state, X being separated at a large distance from YZ . The curve obtained in the manner described above, and which is a section through the potential-energy surface at the activation point, may be called a "potential-energy profile."

Factors Affecting Form of Potential-energy Profile.²⁸—From an examination of Fig. 44, it can be seen that the value of the activation energy is determined by four factors which will be discussed in turn; they are

1. The strength of the bond broken $Y-Z$.
2. The repulsion energy between X and YZ .
3. The repulsion energy between XY and Z .
4. The strength of the bond $X-Y$.

1. The stronger the bond $Y-Z$, the greater the energy of dissociation of the molecule YZ and hence the higher will be the energy level to which the right-hand side of I becomes asymptotic. This means that, the greater the strength of the $Y-Z$ bond, the steeper will be the curve I and hence the higher the activation energy, since the curves I and II will now intersect at a higher energy level.

2. The effect of the repulsion energy between X and YZ , as already seen, is to raise the potential-energy curve from I' to I ; the greater the repulsion, the higher the position of the curve and so the greater will be the activation energy.

3. An increase in the repulsion energy between XY and Z will have the effect of making the curve II rise more rapidly as the distance $Y-Z$ is diminished, and this will bring about an increase in the energy of activation.

4. The position of curve II' is determined by the potential energy of XY in its equilibrium state and hence by the heat of dissociation of the molecule, or, in other words, by the strength of the $X-Y$ bond. The greater the strength of this bond, the

²⁸ Evans and Polanyi, Ref. 26; see also C. N. Hinshelwood, K. J. Laidler and E. W. Timm, *J. Chem. Soc.*, 848 (1938).

lower will be the potential energy of XY. The difference in level between II and II' is small, being equivalent to the energy required to stretch the X—Y bond from the equilibrium separation to that in the activated state; and so the position of curve II is determined almost entirely by the X—Y bond strength. An increase in this factor will result in a vertical lowering of II, and hence a decrease in activation energy.

It is evident, therefore, that positive increments in the factors 1, 2 and 3 should increase the activation energy for a reaction of the type under consideration, whereas an increase in 4 will produce the opposite effect. The first three of these factors

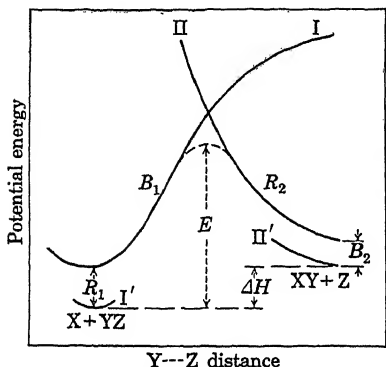


Fig. 45.—Potential-energy curves showing repulsion and bond energies. (*Ogg and Polanyi*.)

have been classified as the “inertia” and the last as the “driving force” of a chemical reaction. The resonance effect will, of course, help to lower the activation energy in any case, and this lowering will be greater the larger the value of the exchange integral H_{AB} .

Construction of Potential-energy Profiles.²⁹—By neglecting the resonance energy, it is possible, in many cases, to draw an approximate potential-energy profile for a reaction

from empirical data, without the necessity of making any assumption as to the division of the bond energies into coulombic and exchange contributions. Since the reaction will tend to follow the most favorable path, it is necessary to consider only a linear configuration of the three atoms involved; as already seen (page 90), the potential energy of the system under these conditions is a minimum. Taking into consideration the four factors that determine activation energy, if resonance is neglected, definite significance can be given to the position and nature of the curves making up the energy profile. The potential-energy levels of the initial and final state, *i.e.*, YZ in the normal state with X at infinity and XY in the normal state with Z at infinity, are indicated by the horizontal lines I' and II', respectively, in

²⁹ See Ref. 26.

Fig. 45. The difference between them is equal to the heat change accompanying the reaction under consideration, *i.e.*, ΔH at constant pressure or ΔE at constant volume. Curve I, which gives the variation of bond energy B_1 of YZ, is raised above I' by R_1 , the repulsion energy between X and YZ, and curve II for the repulsion energy R_2 between XY and Z is raised above II' by B_2 , which is the energy of stretching the X—Y bond. The potential energy of the system having the bond assignments of the initial state is thus given by $R_1 + B_1$, and that with the bonds as in the final state by $R_2 + B_2$; the point where the two curves cross then gives the activated state, from which the energy of activation E may be obtained.

For a homopolar diatomic molecule the bond energy is given by the appropriate Morse equation; and, for an ionic compound, use may be made of equations of the form

$$B = -\frac{\varepsilon^2}{r} + \frac{\tau}{r^\rho} \quad (56)$$

or

$$B = -\frac{\varepsilon^2}{r} + br^{-9}, \quad (57)$$

in which the first term on the right-hand side gives the coulombic attraction between singly-charged ions and the second term represents the repulsion energy of their two inert-gas-like shells. In these equations, ε is the electronic charge and r is the internuclear separation; the constant b is determined by the condition that dB/dr is equal to zero when r is equal to r_0 , the normal internuclear separation. The constant ρ in Eq. (56) may be taken as 0.345×10^{-8} cm. The repulsion energy can be calculated³⁰ by means of the equation

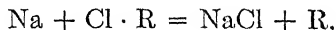
$$R = br^{-9} - cr^{-6} \quad (58)$$

where b has a significance similar to that of the same term in Eqs. (56) and (57) and cr^{-6} , which is negligibly small at distances of the order of those existing in the activated state, is due to the van der Waals attraction. If one of the reacting species is an ion and the other a molecule or radical, then an electrostatic attractive term $-\alpha\varepsilon^2/2r^4$ must be included; the quantity α is

³⁰ Cf. M. Born and J. E. Mayer, *Z. Physik*, **75**, 1 (1934).

the polarizability of the molecule or radical. The potential-energy curves for $R_1 + B_1 (= E_A)$ and $R_2 + B_2 (= E_B)$, having been drawn with the distance Y—Z as ordinate, the relative positions are fixed by the fact that the difference in level between I' and II' in Fig. 45 is equal to the heat evolved in the reaction. Applications of this approximation method for deriving activation energies will be found in Chap. V.

The Repulsion Energy.³¹—In certain cases, *e.g.*, reactions of the type



where R is an alkyl radical, it appears that the energy of repulsion of the reactants is very small; for example, a sodium atom can apparently approach a chlorine atom, held by a homopolar bond to another atom, up to the normal distance of the ions in sodium chloride without undergoing appreciable repulsion. In reactions for which this is true, the term R_1 can be neglected and the calculations are consequently simplified; hence, it is of interest to see under what conditions the repulsion energy becomes small. Equation (53) for the potential energy, omitting resonance energy, *i.e.*, when β and γ are small, may be written

$$E_A = A + B + C + [\alpha - \frac{1}{2}(\beta + \gamma)], \quad (59)$$

where A , B and C are the coulombic energies of the three possible diatomic molecules, YZ, XY and XZ, respectively. The quantity $A + \alpha$ represents the total bond energy B_1 of YZ, and hence the remaining terms $B + C - \frac{1}{2}(\beta + \gamma)$ must be equal to the repulsion energy R_1 . For this to be small, it is clear either that B , C , β and γ must all be small or that

$$B + C \approx \frac{1}{2}(\beta + \gamma).$$

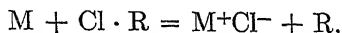
If the coulombic energy is 33 per cent of the total, this condition is satisfied; and hence it is probable that the repulsion energy is small when the essential reaction occurs between electrons whose principal quantum numbers are 3 (*cf.* Table IV, page 84).

Heats of Reaction and Energy of Activation.³²—The assumption that the energy of repulsion is small leads to interesting con-

³¹ Ogg and Polanyi, Ref. 26; Evans and Warhurst, Ref. 26.

³² J. Horiuti and M. Polanyi, *Acta Physicochim. U.R.S.S.*, **2**, 505 (1935); Ogg and Polanyi, Ref. 26; Evans and Polanyi, Ref. 26.

clusions concerning parallel changes in energies of activation and heat changes in certain reactions of an analogous type. Consider for example, the reaction



where M is an alkali metal and R is an alkyl radical; if the repulsion between M and $Cl \cdot R$ is small, as is probable, then curve I (Fig. 45) will be the same irrespective of the nature of the alkali metal. The *slope* of the repulsion curve II will also be the same in each case,* but its position on the energy scale will depend on the heat change accompanying the particular reaction. Two curves IIa and IIb for the alkali metals, designated by M_a and M_b , respectively, are shown in Fig. 46. If the binding energies of the ions are not very different, then it follows that the difference in the heats of reaction is given by ΔQ , as shown; the corresponding change in the activation energy is ΔE . There is evidently a relationship between the two quantities

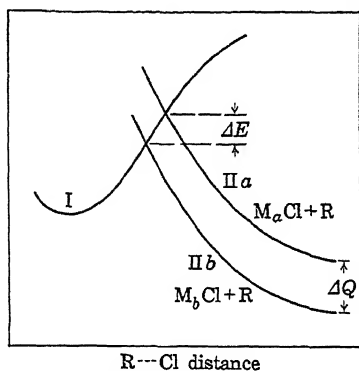


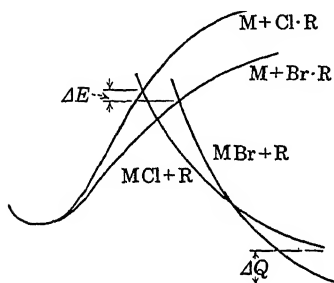
FIG. 46.—Potential-energy curves for reaction between two different alkali metals and $R \cdot Cl$. (Evans and Polanyi.)

which can be taken as $\Delta E = x \Delta Q$, where x lies between zero and unity. It is to be expected, therefore, that for the series of reactions of Li , Na , K , etc., with a given halide, *e.g.*, $R \cdot Cl$, the energies of activation should follow the same order as the heats of reaction. This general rule will also hold if the alkali metal and the halogen remain unchanged while the radical R is varied; in these circumstances, curve II (Fig. 45) is almost unaffected because the repulsion is essentially between the halogen atom and the carbon of the radical R , but the position of I, which depends on the strength of the $R-Cl$ bond, varies. It is apparent that if one of the lateral atoms, *i.e.*, M or R , in the reaction $M + Cl \cdot R$, is varied there should be a parallelism between the heat change and the energy of activation; but if the

* It should be observed that the repulsion between Cl^- (of M^+Cl^-) and the radical R is not negligible.

central atom, *i.e.*, Cl, is changed, this parallelism does not necessarily exist. This may be seen from Fig. 47; the curve for the strength of binding of halogen to the radical R is altered in shape, and there is also a change in the shape and position of the repulsion curve. In the particular case shown the heats of reaction and energies of activation change in opposite directions. The former increases in going from Cl to Br, whereas the latter decreases, as has been actually observed for the reactions

between CH_3Cl and CH_3Br ,
and $\text{C}_6\text{H}_5\text{Cl}$ and $\text{C}_6\text{H}_5\text{Br}$
vapors with sodium vapor.³³



Distance $\text{M} \cdots \text{Cl}$ (or Br)

FIG. 47.—Potential-energy curves for reaction between an alkali metal and either $\text{R}\cdot\text{Cl}$ or $\text{R}\cdot\text{Br}$. (Evans and Polanyi.)

THE TRANSMISSION COEFFICIENT

The possibility that systems with sufficient energy to reach the activated state may be reflected back to the initial state on account of the curvature of the potential-energy surface has been already noted (page 103); it is necessary now to examine this

subject in further detail. As the problems are distinct, it is convenient to consider separately adiabatic reactions, *i.e.*, processes that take place entirely on one potential-energy surface, and nonadiabatic reactions, where there is a possibility of passing from one surface to another.

Adiabatic Reactions.—Suppose that for an adiabatic reaction the system of reactants and resultants is in complete thermal equilibrium; equal numbers of systems at the top of the energy barrier, *i.e.*, in the activated state, will then be passing from the first valley to the second and from the second valley to the first. Of the systems moving from the first valley, *i.e.*, the initial state, to the second valley, *i.e.*, the final state, at equilibrium, a fraction κ only will have come originally from the initial state and will proceed directly to the final state without returning to

³³ M. Polanyi *et al.*, *Z. physik. Chem.*, **B**, 11, 97 (1930); *Trans. Faraday Soc.*, **32**, 633 (1936); F. Fairbrother and E. Warhurst, *ibid.*, **31**, 987 (1935); J. L. Tuck and E. Warhurst, *ibid.*, **32**, 1501 (1936).

the initial state. The fraction κ is called the "transmission coefficient"; it is important in connection with the statistical theory of reaction rates to be described in Chap. IV and applied in later chapters. Suppose the initial, activated and final states are represented in Fig. 48; let A be the number of systems arriving in unit time at the activated state *directly* from the initial state and B the number coming *directly* from the final state, and suppose ρ_i and ρ_f are the probabilities of reflection from left to right and from right to left, respectively. The resulting condition is then shown in Fig. 48.³⁴ On the assumption that the

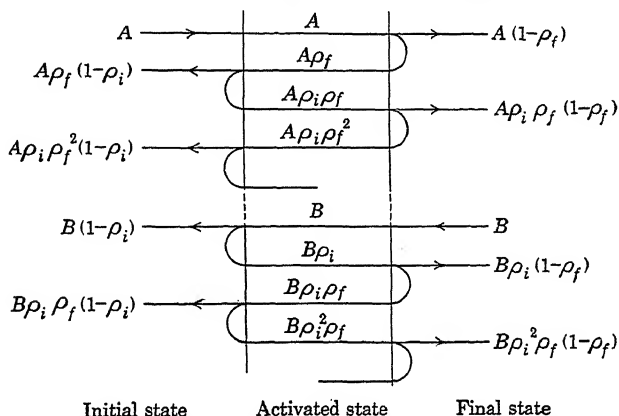


FIG. 48.—Calculation of transmission coefficient. (Hirschfelder and Wigner.)

probability of crossing is independent of the number of times the system has previously passed through the activated state, it is readily seen that the numbers of crossings of the activated state from left to right ($N_{l \rightarrow r}$) and from right to left ($N_{r \rightarrow l}$) are given by

$$N_{l \rightarrow r} = A(1 + \rho_i\rho_f + \rho_i^2\rho_f^2 + \cdots) + B\rho_i(1 + \rho_i\rho_f + \rho_i^2\rho_f^2 + \cdots) \quad (60)$$

$$= (A + B\rho_i)(1 - \rho_i\rho_f)^{-1}. \quad (61)$$

$$N_{r \rightarrow l} = A\rho_f(1 + \rho_i\rho_f + \rho_i^2\rho_f^2 + \cdots) + B(1 + \rho_i\rho_f + \rho_i^2\rho_f^2 + \cdots) \quad (62)$$

$$= (A\rho_f + B)(1 - \rho_i\rho_f)^{-1}. \quad (63)$$

At thermal equilibrium the number crossing in one direction is equal to the number going in the other direction, i.e.,

$$N_{l \rightarrow r} = N_{r \rightarrow l},$$

³⁴ J. O. Hirschfelder and E. Wigner, *J. Chem. Phys.*, **7**, 616 (1939).

and hence from Eqs. (61) and (63)

$$B = A(1 - \rho_f)(1 - \rho_i)^{-1}. \quad (64)$$

Substituting the value of B from Eq. (64) in (61) gives

$$N_{i \rightarrow r} = A(1 - \rho_i)^{-1}. \quad (65)$$

The number of systems that have originated in the initial state and proceed to the final state ($N_{i \rightarrow f}$), without returning to the initial state, is

$$N_{i \rightarrow f} = A(1 - \rho_f)(1 + \rho_i \rho_f + \rho_i^2 \rho_f^2 + \dots) \quad (66)$$

$$= A(1 - \rho_f)(1 - \rho_i \rho_f)^{-1}. \quad (67)$$

By definition, the transmission coefficient κ is equal to $N_{i \rightarrow f}/N_{i \rightarrow r}$; and so, from Eqs. (65) and (67), it is seen that

$$\kappa = \frac{(1 - \rho_i)(1 - \rho_f)}{(1 - \rho_i \rho_f)}. \quad (68)$$

For the transmission coefficient to approach unity, therefore, it is necessary that the reflection probabilities ρ_i and ρ_f should both be small; *i.e.*, the probability of returning to the initial or final state after having passed through the activated state must be small. By use of Eq. (68) as the basis for wave-mechanical treatment, it has been shown that, for a system having several degrees of freedom, κ is affected by the interchange of translational and vibrational energy, *i.e.*, by the curvature of the valley, as might be expected. If the vibrational motion is rapid, however, compared with the motion along the reaction path, it is probable that the transmission coefficient will be of the order of unity.

Nonadiabatic Reactions.—When the resonance energy in the activated state is small, the upper and lower surfaces, into which the potential-energy surfaces for initial and final states split (*cf.* page 137), approach each other closely. There will then be a relatively large probability that the activated complex will pass from the lower to the upper surface (path *a*, Fig. 49), instead of continuing along the coordinate of decomposition (path *b*). The result will be that a smaller proportion of the systems coming from the initial state will pass directly to the final state, *i.e.*, the transmission coefficient will be smaller, than

if the transition from one surface to another were not possible. Reactions in which there is a relatively large probability of crossing from the lower to the upper potential-energy surface are called "nonadiabatic." They generally occur when the reaction is accompanied by an electronic transition, *e.g.*, a change of multiplicity; the eigenfunctions of initial and final states then do not overlap to any appreciable extent, and the resonance energy resulting from the mutual interaction of the electronic systems (page 137) is negligible. Although nonadiabatic reactions are probably always accompanied by an electron switch, the reverse is not necessarily true. It is possible, as, for example, in the decomposition of nitrous oxide (page 333), that appreciable resonance may occur in the activated state as the result of other forms of interaction which are normally so small that they can be neglected.

It will be seen in Chap. VI, where reactions involving electronic transitions are considered, that the transmission coefficient is related to the probability of the reacting system remaining on the lower surface. The question of the probability of *crossing* (χ) from one surface to another has been considered by L. Landau³⁵ and by C. Zener.³⁶ Zener derived the following expression for this probability:

$$\chi = e^{-4\pi^2\epsilon^2/hv|s_i - s_f|}; \quad (69)$$

where 2ϵ is the energy equivalent of the least distance of separation between the upper and lower surfaces, and hence ϵ is the resonance energy in the activated state; v is the velocity with which the system passes through this configuration; and $|s_i - s_f|$ is the absolute magnitude of the difference between the slopes of the two common tangents to the surfaces. This equation holds only if $\epsilon \ll \frac{1}{2}\mu v^2$ where μ is the reduced mass of the system.

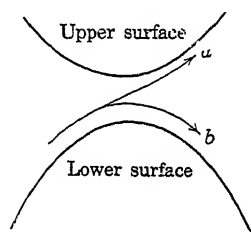


FIG. 49.—Crossing from lower to upper potential-energy surface in a nonadiabatic reaction.

³⁵ L. Landau, *Phys. Z. Sowjetunion*, **1**, 88 (1932); **2**, 46 (1932).

³⁶ C. Zener, *Proc. Roy. Soc.*, **137**, A, 696 (1932); **140**, A, 660 (1933).

The probability of *remaining* (ρ) on the lower surface is equal to $1 - \chi$, and so it follows that

$$\rho = 1 - e^{-4\pi^2\epsilon^2/\hbar v|s_i - s_f|}. \quad (70)$$

If the resonance energy ϵ is small, the exponential may be expanded and all terms beyond that involving ϵ^2 can be neglected, so that

$$\rho = \frac{4\pi^2\epsilon^2}{\hbar v|s_i - s_f|}. \quad (71)$$

If there is no appreciable overlap in the eigenfunctions of the initial and final states, *i.e.*, if the normal electrostatic-interaction terms in the Hamiltonian operator do not make any appreciable contribution to the energy, the quantity ϵ in Eq. (69) must arise from perturbation terms in the Hamiltonian resulting from magnetic and similar interactions (*cf.* page 336). If ϵ were known, it would be possible to calculate ρ or χ ; it is desirable, however, to average the results over all the velocities, or more strictly over all the momenta p , of the system. The mean value of ρ is, therefore, given by ³⁷

$$\bar{\rho} = \frac{\int_0^\infty \rho e^{-p^2/2\mu kT} dp}{\int_0^\infty e^{-p^2/2\mu kT} dp}. \quad (72)$$

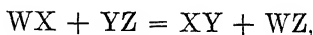
From Eq. (72) it is possible to evaluate $\bar{\rho}$ by numerical integration in terms of $4\pi^2\epsilon^2\mu^{1/2}/(2kT)^{3/2}|s_i - s_f|$. The actual value of $\bar{\rho}$, and hence of the transmission coefficient, depends both on the magnitude of the resonance energy ϵ and on the $|s_i - s_f|$ term; in general, $\bar{\rho}$ increases as ϵ increases, and if the latter exceeds $\frac{1}{2}kT$ per molecule, then $\bar{\rho}$ approximates to unity and almost all the systems remain on the lower surface.

EMPIRICAL RULES FOR ACTIVATED STATE

Although the complete calculation of the potential-energy surface is the only satisfactory way of arriving at the properties of the activated state, it is possible to make approximate estimates of the activation energy and of the dimensions of the activated complex by purely empirical methods. It has been

³⁷ A. E. Stearn and H. Eyring, *J. Chem. Phys.*, **3**, 778 (1935); see also M. G. Evans and E. Warhurst, *Trans. Faraday Soc.*, **35**, 593 (1939).

found, for example, that in the activated molecule the length of a bond is increased by about 10 per cent of its normal value, and so in the absence of more precise information this approximate generalization may be employed to obtain the dimensions of the activated complex. For a reaction of the type



which is written in the exothermic direction, the energy of activation has been found to be approximately one-fourth the sum of the energies of the W—X and Y—Z bonds. If D_{W-X} and D_{Y-Z} are the heats of dissociation of the diatomic molecules WX and YZ, respectively, then

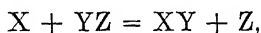
$$E = \frac{1}{4}(D_{W-X} + D_{Y-Z}). \quad (73)$$

Some examples of the application of this rule are given in Table V; the agreement between calculated and experimental activation energies is seen to be fairly good.

TABLE V.—EMPIRICAL DERIVATION OF ACTIVATION ENERGIES

Reaction	Activation energy, kcal.	
	Calc.	Obs.
$H_2 + I_2 = 2HI$	40	40
$H_2 + Br_2 = 2HBr$	43	>43
$H_2 + H_2 = H_2 + H_2$	52	>57
$I_2 + Cl_2 = 2ICl$	26	>15
$H_2 + ICl = HI + HCl$	42	>34

The activation energies of three-center reactions, *viz.*,



are generally small in the exothermic direction, particularly if X is a hydrogen atom. The values lie between zero and 10 kcal.; and since the energy of the Y—Z bond is of the order of 50 to 100 kcal., it is evident that the activation energy is approximately 5 per cent of the strength of the bond broken in the exothermic direction. If the interaction between the distant atoms X and Z is neglected, the London equation leads to the conclusion that the activation energy is a definite fraction, depending on the

proportions of coulombic and resonance energies, of the energy of the Y—Z bond. If the coulombic energy is taken to be 14 per cent of the total binding energy, the activation energy is found to be $0.055D'$, where D' is the dissociation energy plus the zero-point energy of the diatomic molecule YZ.³⁸ For an endothermic reaction the activation energy is obtained by adding the heat of reaction to the activation energy for the reverse, *i.e.*, exothermic, process. The values obtained by taking 5.5 per cent of the dissociation energy for reactions involving atomic hydrogen are in agreement with the experimental results; but since the latter are in any case small, any fraction between zero and 10 per cent would be almost equally satisfactory on the whole. For reactions involving sodium and other atoms the energies of activation are considerably larger than those given by the empirical rule.

It is of interest to call attention here to the fact that the energy of activation is, in general, considerably less than the energy required to break the bonds in the reacting molecules. The reason for this is that new bonds are formed in the activated state, and the energy of activation is the difference between the energy obtained by the formation of these bonds and the amount necessary to break the bonds in the reactants.

³⁸ J. O. Hirschfelder and F. Daniels, unpublished.

CHAPTER IV

STATISTICAL TREATMENT OF REACTION RATES

THE DISTRIBUTION OF ENERGY

Postulates of Statistical Mechanics.¹—The basis of statistical mechanics is the determination of the probability of the occurrence of any particular state of a system. The prediction of the exact behavior of a single gas molecule appears impossible, but by means of statistical methods the average behavior of an ensemble consisting of a large number of such molecules can be determined. The results so obtained have found application in many aspects of physics and chemistry, but a limited treatment only will of necessity be given, sufficient for the purpose of developing a theory of reaction rates. The fundamental equations originally obtained by Maxwell, Boltzmann and others can be derived in various ways, but the method employed here will be based on the elementary considerations of quantum mechanics as presented in a previous chapter. The essential postulates are: (1) The amount of energy in the system is constant; *i.e.*, there is conservation of energy. (2) The number of particles is constant. (3) There exist definite energy levels (or quantum states) as required by quantum mechanics. (4) All possible levels (states) for the entire system, consistent with the previous postulates, have equal a priori probability; *i.e.*, each state corresponding to one linear independent wave function is to be given the same weight.

A Particle in a Box.—Imagine a single particle, such as a gas molecule, inside a rectangular box, the length, height and breadth of which are a , b and c , respectively (Fig. 50). Inside the box

¹ For detailed treatment, see R. H. Fowler, "Statistical Mechanics," Cambridge University Press, 1936; R. C. Tolman, "The Principles of Statistical Mechanics," Oxford University Press, 1938; R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, 1939; J. E. Mayer and M. G. Mayer, "Statistical Mechanics," Wiley, 1940.

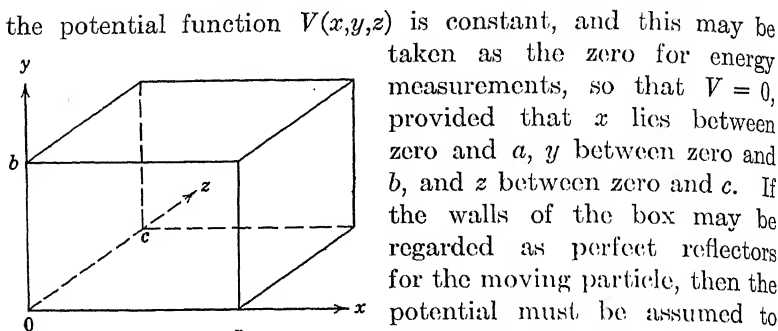


FIG. 50.—Rectangular box containing a gas molecule.

taken as the zero for energy measurements, so that $V = 0$, provided that x lies between zero and a , y between zero and b , and z between zero and c . If the walls of the box may be regarded as perfect reflectors for the moving particle, then the potential must be assumed to increase suddenly to infinity at the boundaries. Assuming that

the particle, of mass m , may be treated as obeying the wave equation, it follows (see page 52) that

$$-\frac{h^2}{8\pi^2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = (E - V)\psi; \quad (1)$$

and since V is zero within the box,

$$\frac{h^2}{8\pi^2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = E\psi \quad (2)$$

where ψ is a function of the coordinates x , y and z .

It is desirable to separate the three variables, and this can be done if the assumption is made that ψ can be represented by

$$\psi = X(x)Y(y)Z(z), \quad (3)$$

where X is a function of x only, Y of y only, and Z of z only. Dividing Eq. (2) through by ψ and then substituting in Eq. (3) yields

$$-\frac{h^2}{8\pi^2m} \left(\frac{1}{X} \cdot \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \cdot \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \cdot \frac{\partial^2 Z}{\partial z^2} \right) = E. \quad (4)$$

Since X is a function of x alone, the term involving X does not change when y and z are altered; similarly, the term with Y is independent of x and z , and that containing Z does not vary as x and y are changed. The sum of the three terms must, however, always remain constant and equal to E , after multiplication by the factor $(-h^2/8\pi^2m)$. It follows, therefore, that if y and z are kept constant, the value of $(1/X)(\partial^2 X/\partial x^2)$ must remain

unchanged in spite of variations in x ; since this term is independent of y and z , it is evident that it must be a constant. The same argument applies to the analogous terms involving y and z , each of which is equal to a constant quantity. It is possible, therefore, to divide E into three constant parts, *viz.*, E_x , E_y and E_z , corresponding to the energies parallel to the three coordinates, so that Eq. (4) can be split up into three equations of the same form; thus, the one in x may be written

$$\frac{\hbar^2}{8\pi^2m} \left(\frac{1}{X} \cdot \frac{\partial^2 X}{\partial x^2} \right) = E_x \quad (5)$$

and its general solution is

$$X = C \sin (Ax + B), \quad (6)$$

where A , B and C are constants. The probability of finding the particle at any point within the box is given by the square of the absolute value of the function ψ at that point (*cf.* page 31); hence, X^2 , being a function of the coordinate x only, is a measure of the probability of the particle being in some position along the x -axis. The probability that the particle should be in the walls is zero; and so it follows that X must be zero for $x = 0$ and $x = a$, these being the x -coordinates for the two walls perpendicular to the x -axis. These conditions can be satisfied only if

$$A = \frac{n_x\pi}{a} \quad \text{and} \quad B = 0, \quad (7)$$

where n_x must be an integer; it follows, therefore, that to represent a satisfactory solution of Eq. (5) the function X , as given by Eq. (6), must be

$$X = C \sin \frac{n_x\pi}{a} x. \quad (8)$$

Substitution of this value of X in Eq. (5) now gives

$$E_x = \frac{n_x^2 \hbar^2}{8a^2m}, \quad (9)$$

where n_x may be regarded as the quantum number that determines the possible values of the energy of the particle parallel to the x -axis. Analogous equations may be derived for the

energies E_y and E_z which depend on the coordinates y and z , respectively; thus,

$$E_y = \frac{n_y^2 h^2}{8b^2 m} \quad \text{and} \quad E_z = \frac{n_z^2 h^2}{8c^2 m}. \quad (10)$$

These equations give the permitted levels of translational energy, along the three rectangular coordinates, of a particle in a box. In actual practice, for gases the three quantities corresponding to $h^2/8a^2m$ are so small, *i.e.*, the separation of successive energy levels is so minute, that the distribution of energy may be regarded as continuous. It is for this reason that under ordinary conditions translational energy may be treated by classical methods without any appreciable error.

Energy Levels and Degrees of Freedom.-- Ignoring the question of the magnitude of the energy separations for the present, it is seen from Eq. (10) that when the quantum number is n_x the energy in the x -direction is $E_x(n)$; *i.e.*, there are n quantum levels, or states, for energies lying between zero and $E_x(n)$. According to Eq. (10), n is proportional to $E_x^{1/2}(n)$, so that the number of levels L_1 with energy from 0 to E , in one direction, *i.e.*, in one degree of freedom, is given by

$$L_1 \propto E^{1/2}. \quad (11)$$

If the energy E is in two degrees of freedom, *e.g.*, x and y , that is, if two quantum numbers n_x and n_y are required to specify it, then

$$E = E_x + E_y = \frac{n_x^2 h^2}{8a^2 m} + \frac{n_y^2 h^2}{8b^2 m} \quad (12)$$

$$= \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} \right) \quad (13)$$

$$= \frac{h^2}{8m} l^2, \quad (14)$$

where

$$l^2 = \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}. \quad (15)$$

The number of quantum levels, with energy from 0 to E in two degrees of freedom, can be conveniently studied by imagining a system of two Cartesian coordinates and plotting n_x/a and n_y/b ,

respectively, in the two directions. For each positive integral value of n_x and n_y , there will be a point on the diagram corresponding to a definite quantum state in two degrees of freedom. If the energy of the system is not to exceed E , then by Eq. (15) the values of n_x and n_y must be such that

$$\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} \leq l^2, \quad (16)$$

and every point in Fig. 51 satisfying this requirement represents a possible quantum level for energy between zero and E in two degrees of freedom. The total number of such points is obtained by drawing the quadrant of a circle of radius l , having its center at the origin of Fig. 51; all the points in the quadrant satisfy Eq. (16), and hence the required number of quantum levels (L_2), is proportional to its area, which is $\frac{1}{4}(\pi l^2)$. It follows, therefore, that

$$L_2 \propto l^2, \quad (17)$$

and hence, by Eq. (14),

$$L_2 \propto E, \quad (18)$$

for energy in two degrees of freedom.

If the energy is in three degrees of freedom, then

$$E = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad (19)$$

$$= \frac{h^2}{8m} l^2, \quad (20)$$

where

$$l^2 = \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}. \quad (21)$$

All quantum states with energy lying between zero and E must satisfy the condition

$$\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \leq l^2. \quad (22)$$

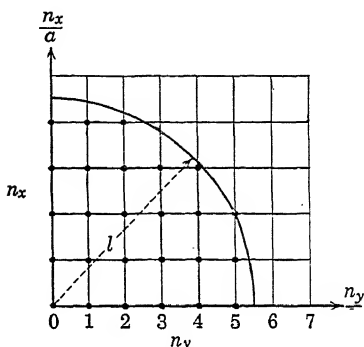


FIG. 51.—Representation of translational quantum levels in two degrees of freedom.

It can be readily seen that the number of quantum states for which this holds can be obtained by making a three-dimensional plot of n_x/a , n_y/b and n_z/c and counting the number of points for which n_x , n_y and n_z are integral, lying within the octant of a sphere of radius l ; i.e.,

$$L_3 \propto l^3, \quad (23)$$

and hence, by Eq. (20),

$$L_3 \propto E^{3/2}. \quad (24)$$

The argument can be extended to any number of degrees of freedom; and a comparison of Eqs. (11), (18) and (24) shows that, in general, the number of quantum states L_s with energy between 0 and E in s degrees of freedom is given by

$$L_s \propto E^{1/2s} \quad (25)$$

The number of levels dL_s of energy between E and $E + dE$ can be obtained by differentiating Eq. (25) with respect to E , so that

$$dL_s = \text{const.} \times \frac{s}{2} E^{1/2s-1} dE \quad (26)$$

$$= \text{const.} \times E^{1/2s-1} dE, \quad (27)$$

since $\frac{1}{2}s$ is constant.

Particles as Thermometer.†—It is necessary to consider next a box containing N particles, each of which has energy of translation in three degrees of freedom. Since each particle requires three quantum numbers for its complete description, the N particles‡ will require $3N$ quantum numbers. The number of states for which the total translational energy lies between zero and E is thus proportional to $E^{3/2}N$. Let the particles under consideration be N noninteracting molecules, and suppose an additional molecule is added to the box. If the total energy of the $N + 1$ molecules is W , then the probability $P(w)$ that the precise amount of energy w shall be uniquely in the extra molecule is simply equal to the probability that the remaining N molecules shall have energy $W - w$ in $3N$ degrees of freedom.

* For the detailed calculations of the volume enclosed by a hypersphere or hyperellipsoid in n -dimensional space, see R. C. Tolman, "Statistical Mechanics," p. 128, Chemical Catalog Co., Inc., 1927.

† E. U. Condon, *Phys. Rev.*, **54**, 937 (1938).

‡ It will be convenient, for the present, to think of the particles as being unlike; the effect of like particles in requiring the introduction of symmetry considerations will be discussed shortly.

This is a consequence of the postulate that, provided that the energy remains constant, all possible quantum states have equal probability. The required probability $P(w)$ is virtually identical with that for the N molecules to have translational energy between $W - w$ and $W - w + dw$ and is consequently equal to the "concentration" or "thickness" of quantum levels, *i.e.*, dL/dw , in the vicinity of the energy $W - w$. This quantity is given by the appropriate form of Eq. (27), it being noted that E is now $W - w$ and s is $3N$; thus,

$$dL = \text{const.} \times (W - w)^{\frac{3}{2}N-1} dw, \quad (28)$$

and hence,

$$P(w) = \frac{dL}{dw} = \text{const.} \times (W - w)^{\frac{3}{2}N-1}. \quad (29)$$

If, instead of the energy w being present in the additional molecule in a unique manner, there are g levels or quantum states corresponding to this amount of energy, the probability $P(w)$ will now be g times as great; thus,

$$P(w) = \text{const.} \times g(W - w)^{\frac{3}{2}N-1}. \quad (30)$$

Upon dividing through the right-hand side by W , which is constant, it is seen that

$$P(w) = \text{const.} \times g \left(1 - \frac{w}{W}\right)^{\frac{3}{2}N-1}. \quad (31)$$

Expanding the quantity $(1 - w/W)^{\frac{3}{2}N-1}$ by means of the binomial theorem and making use of the fact that $3N$ is large and w/W is small, it is found that Eq. (31) reduces to the form

$$P(w) = \text{const.} \times g e^{-3Nw/2W}. \quad (32)$$

On substituting γ for the constant quantity $2W/3N$, which is the average energy of a molecule in two translational degrees of freedom, it is seen that

$$P(w) = \text{const.} \times g e^{-w/\gamma}. \quad (33)$$

The argument developed above is applicable irrespective of the nature of the energy w ; it may be nuclear, electronic, vibrational, rotational or translational. It will be seen shortly that the quantity γ in Eq. (33) is related to the temperature of the system, so

that the N molecules behave effectively as an ideal gas thermometer for maintaining the temperature of the system in equilibrium with the single molecule under consideration

It is thus possible to write

$$P(\epsilon_i) = \text{const.} \times g_i e^{-\epsilon_i/\gamma} \quad (34)$$

for the probability that a molecule shall have energy ϵ_i of a particular kind designated by i . The degeneracy g_i is generally called the "statistical weight" or "a priori probability" of the state. For a nondegenerate level, g_i is unity, and Eq. (34) becomes

$$P(\epsilon_i) = \text{const.} \times e^{-\epsilon_i/\gamma}. \quad (35)$$

If the energy ϵ_i is translational, it is convenient to write in place of g_i , *i.e.*, the number of quantum states for the single molecule whose energy lies between w and $w + dw$, the number of levels dL as given by Eq. (27) in the requisite degrees of freedom. For three degrees of freedom, it follows, therefore, that

$$g = dL_3 = \text{const.} \times \epsilon^{1/2} d\epsilon, \quad (36)$$

and, hence, the probability that a molecule will have translational energy between $(\epsilon)_3$ and $(\epsilon + d\epsilon)_3$ in three degrees of freedom is

$$P(\epsilon)_3 = \text{const.} \times e^{-\epsilon/\gamma} \epsilon^{1/2} d\epsilon. \quad (37)$$

For one degree of freedom, dL_1 is $\epsilon^{-1/2} d\epsilon$ and so

$$P(\epsilon)_1 = \text{const.} \times e^{-\epsilon/\gamma} \epsilon^{-1/2} d\epsilon.$$

The Maxwell-Boltzmann Equation.—Before proceeding further, the significance of the constant γ appearing in the probability equations must be investigated. To do so, consider the N molecules in a rectangular box of volume v . The pressure on the walls of the box is due to the bombardment of the molecules which are moving in all directions; since no direction is preferred over any other, the pressure on any one face of the box, *e.g.*, that perpendicular to the x -axis, which will be the same as that on the others, may be regarded as due to the x -component of the velocities of all the molecules. If \bar{x} is the root mean square velocity component in the x -direction, the mean change of momentum from impact of a single molecule under consideration is $2m\bar{x}$.

The molecules within a distance \bar{x} would reach each square centimeter of the wall in unit time. Since there are N molecules in the volume v , it follows that $N\bar{x}/v$ molecules strike the wall in unit time. The rate of change of momentum per square centimeter of wall is thus $2mN\bar{x}^2/v$, and this, by definition, must equal the pressure exerted by the molecules; thus,

$$p = 2mN\bar{x}^2 \quad (39)$$

The value of \bar{x}^2 may be derived with the aid of Eq. (38); remembering that the translational, *i.e.*, kinetic, energy in one degree of freedom, *e.g.*, parallel to the x -axis, may be represented by $\frac{1}{2}m\bar{x}^2$, it follows that the probability of a molecule having a velocity between \dot{x} and $\dot{x} + d\dot{x}$, in a particular direction, is

$$P(\dot{x})_1 = \text{const.} \times e^{-\frac{1}{2}m\dot{x}^2/\gamma} d\dot{x}. \quad (40)$$

The mean value of \bar{x}^2 is then given by

$$\bar{x}^2 = \frac{\int_0^\infty e^{-\frac{1}{2}m\dot{x}^2/\gamma} \dot{x}^2 d\dot{x}}{\int_{-\infty}^\infty e^{-\frac{1}{2}m\dot{x}^2/\gamma} d\dot{x}} \quad (41)$$

where the integral in the numerator is taken between 0 and ∞ , since only those molecules moving toward the appropriate face of the box need to be considered, whereas in the denominator the integration between $-\infty$ and ∞ makes allowance for the possibility of motion in both directions. Upon evaluating the integrals, which are standard forms, it follows that

$$\bar{x}^2 = \frac{\gamma}{2m}, \quad (42)$$

and insertion in Eq. (39) gives

$$p = N\gamma \quad (43)$$

The foregoing derivation of the pressure applies to an ideal gas system, which is usually defined as obeying the equation $p = RT/v$ per mole of gas; it is clear, therefore, that γ is equivalent to RT/N , where N is now the Avogadro number, *i.e.*, the

number of molecules in 1 mole. The quantity R/N is the gas constant per molecule; it is given the symbol k and designated the "Boltzmann constant." Upon substituting k in the relationship for γ , there is obtained the result

$$\gamma = kT,$$

and hence the probability equation (33) may be written

$$P(\epsilon) = \text{const.} \times g e^{-\epsilon/kT}. \quad (44)$$

This is the general form of the Maxwell-Boltzmann, or classical, law for the distribution of energy.

Symmetry Restriction.—In the derivation of the probability equations, no account has been taken so far of symmetry considerations; it is important to see if this neglect has any serious consequences. It is found, in actual fact, that different symmetry restrictions lead to three different types of statistics for a system of particles, but under normal conditions the deviations from the results deduced above are negligible. Nevertheless, it is of interest to examine the arguments somewhat further.

Classical Statistics.—Consider, in the first place, a system of n distinguishable elements* whose coordinates may be represented by the symbols q_1, q_2, \dots, q_n , and suppose there are available a number g of eigenfunctions u such that $u_a(q_1), u_b(q_2), \dots, u_g(q_n)$ are the solutions of the wave equations for the n elements. The complete eigenfunction ψ for the whole system may thus be taken as the product of the individual eigenfunctions (cf. page 57); hence, neglecting the normalizing factor, this leads to

$$\psi = u_a(q_1)u_b(q_2) \dots u_g(q_n). \quad (45)$$

If there are no symmetry restrictions and the elements 1, 2, \dots , n are distinguishable, this particular solution corresponds to one eigenstate, *i.e.*, quantum level, of the system. Any change in the assignment of the n elements among the g elementary functions would lead to a new solution and hence to another possible eigenstate for the n elements. Suppose the n distinguishable elements are divided into a series of groups, *viz.*,

* The word element is used here in a general, and not in the chemical, sense.

$n_1, n_2, \dots, n_i, \dots$, in each of which the energy is almost constant, so that

$$n = \sum n_i; \quad (46)$$

then the number of ways of distributing the n elements in such groups is given by

$$n_1! n_2! \cdots n_i! \quad (47)$$

If in the i th group there are available g_i eigenfunctions, *i.e.*, if the group is g_i -fold degenerate, then the n_i elements in this group can be arranged in $g_i^{n_i}$ different ways. The total number of eigenstates, or quantum levels, for the n elements, which is a measure of the probability P of this particular distribution, is thus given by

$$P = \text{const.} \times n! \left(\frac{g_1^{n_1}}{n_1!} \cdot \frac{g_2^{n_2}}{n_2!} \cdots \frac{g_i^{n_i}}{n_i!} \right) \quad (48)$$

$$= \text{const.} \times n! \prod \frac{g_i^{n_i}}{n_i!} \quad (49)$$

where \prod is the sign used for the product of the series of similar terms. Taking logarithms of Eq. (49), it is seen that

$$\ln P = \ln n! + \sum_i (n_i \ln g_i - \ln n_i!) + \text{const.} \quad (50)$$

According to Stirling's formula,

$$\ln x! = (x + \frac{1}{2}) \ln x - x + \frac{1}{2} \ln 2\pi, \quad (51)$$

or, if x is large,

$$\ln x! \approx x \ln x - x, \quad (52)$$

and substitution in Eq. (50), on the assumption that n and n_i are large, gives

$$\ln P = n \ln n + \sum_i (n_i \ln g_i - n_i \ln n_i) + \text{const.}, \quad (53)$$

it being remembered that, by Eq. (46), $\sum_i n_i$ is equal to n . The most probable state is that for which P , or $\ln P$, is a maximum.

For this condition, $\delta \ln P / \delta n_i$ is zero; hence, it follows, by differentiation of Eq. (53), that

$$\sum_i \left(\ln \frac{n_i}{g_i} + 1 \right) \delta n_i = 0, \quad (54)$$

where g_i is taken to be constant. Since the total number of elements n is constant, by the postulate on page 153, then, from Eq. (46),

$$\sum_i \delta n_i = 0. \quad (55)$$

If ϵ_i is the energy of each element in the i th group, then the total energy E is equal to the sum of the energies in all the groups, *i.e.*,

$$E = \sum_i n_i \epsilon_i; \quad (56)$$

and hence, if the conservation of energy is assumed,

$$\delta E = 0 = \sum_i \epsilon_i \delta n_i. \quad (57)$$

To solve Eqs. (54), (55) and (57), the Lagrange method of undetermined multipliers is used, as follows. Multiplying Eq. (55) and (57) by the undetermined constants α and β , respectively, and adding the results to Eq. (54), then

$$\sum_i \left(\ln \frac{n_i}{g_i} + \alpha + \beta \epsilon_i \right) \delta n_i = 0. \quad (58)$$

The variations δn_i are quite arbitrary, and so it follows that the coefficients in Eq. (58) must each equal zero; *i.e.*,

$$\ln \frac{n_i}{g_i} + \alpha + \beta \epsilon_i = 0, \quad (59)$$

$$\therefore n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i}}, \quad (60)$$

or, since α is a constant,

$$n_i = \text{const.} \times g_i e^{-\beta \epsilon_i}. \quad (61)$$

This equation is of the same form as Eqs. (34) and (44); and it can, if necessary, be shown that β is equal to $1/kT$, so that the two equations are really identical. Strictly speaking,

Eq. (61) states that the most probable arrangement of the elements is that in which a number n_i , having energy in the quantum level of ϵ_i , is proportional to $g_i e^{-\epsilon_i/kT}$, whereas according to Eq. (44) the probability that an element will be in the level of energy ϵ_i is given by the same expression. There is, however, no essential difference in the significance of the two equations; and since the conditions specified on page 162 lead to an equation similar to that derived by Maxwell, Boltzmann, etc., they are regarded as forming the basis of classical statistics.

Bose-Einstein Statistics.—In the second case, it may be supposed that there are n particles which are *indistinguishable* and that *symmetric* solutions only are permitted; these postulates lead to the statistics developed by S. N. Bose (1924) and by A. Einstein (1925), and generally known by their names. If, as before, it is supposed that g eigenfunctions are available, the solution of the wave equation for the whole system is not merely as given by Eq. (45), but the complete eigenfunction is the sum of all possible permutations of the n elements among the g eigenfunctions (*cf.* page 58); thus, excluding the normalizing factor,

$$\psi = \sum \mathbf{P} u_a(q_1) u_b(q_2) \dots u_o(q_n). \quad (62)$$

Since symmetric solutions only are possible, there should be no change of sign when the coordinates of two elements are interchanged, and hence it is not necessary to include any positive or negative sign in the summation, as is the case for antisymmetric solutions. Further, in a symmetric eigenfunction, two or more elementary functions may be the same; thus $u_a(q_i)$ may be equal to $u_b(q_i)$, so that there is no restriction as to the number of particles in any quantum state, *i.e.*, associated with any given elementary eigenfunction. To find the number of possible solutions for the whole system, it is necessary first to determine in how many ways n_i particles could be distributed among the g_i eigenfunctions without any restriction as to the number of the particles associated with each particular function. The result may be obtained in the following manner: suppose a box is divided up by means of $g_i - 1$ partitions, giving g_i spaces, in which n_i particles are distributed; then the total number of permutations of the n_i particles and the $g_i - 1$ partitions is $(n_i + g_i - 1)!$ Since the n_i particles are indistinguishable, and

the order of the $g_i - 1$ partitions is immaterial, this result is divided by $n_i!$ and by $(g_i - 1)!$ to give the required number of ways in which n_i particles can be divided between g_i spaces, *i.e.*, g_i eigenfunctions; the required number is thus

$$\frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}. \quad (63)$$

This quantity gives the number of different eigenstates in any group containing n_i particles; but since the whole number n can as before be divided into a set of groups containing $n_1, n_2, \dots, n_i, \dots$ particles,* where n is equal to $\sum_i n_i$, it follows that the total number of quantum levels for the n particles, which is proportional to the probability P of the particular distribution, is

$$P = \text{const.} \times \frac{(n_1 + g_1 - 1)!}{n_1!(g_1 - 1)!} \cdot \frac{(n_2 + g_2 - 1)!}{n_2!(g_2 - 1)!} \dots \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}. \quad (64)$$

$$= \text{const.} \times \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}. \quad (64a)$$

By taking logarithms as before, introducing Stirling's theorem, and assuming n, n_i and g_i to be large, it follows that

$$\ln P = \sum_i [(n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i] + \text{const.}, \quad (65)$$

and differentiation with respect to n_i then gives for the most probable state

$$\sum_i [\ln n_i - \ln (n_i + g_i)] \delta n_i = 0. \quad (66)$$

Introducing the relationships of Eqs. (55) and (57) and using the Lagrange method of undetermined multipliers, as previously, it is found that

$$\sum_i \left(\ln \frac{n_i}{n_i + g_i} + \alpha + \beta \epsilon_i \right) \delta n_i = 0; \quad (67)$$

* Since the particles are now assumed to be indistinguishable, there is only one way of dividing them up into these groups.

and since the coefficients must be zero,

$$n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i} - 1} \quad (68)$$

This equation differs from Eq. (60) of classical statistics by the inclusion of -1 in the denominator, and the modified form should be employed for distinguishable particles having symmetrical solutions of the wave equation, such as, for example, atomic nuclei and atoms containing an even number of unit particles, *viz.*, electrons, protons and neutrons, and also for single photons treated as particles. Provided that the temperature is not too low or the pressure too high, it is permissible to neglect -1 in comparison with the other terms in the denominator, so that the distribution based on Bose-Einstein statistics reduces to the classical form.

Fermi-Dirac Statistics.—The third possibility, equivalent to the statistics of E. Fermi (1926) and of P. A. M. Dirac (1927), is that, as in the previous case, there are n particles which are *indistinguishable* but that *antisymmetric* solutions of the wave equation are the only ones allowed. It follows, therefore, from the arguments developed on page 58, that the eigenfunction for the whole system is, omitting the normalizing factor,

$$\psi = \Sigma \pm P u_a(q_1) u_b(q_2) \cdots u_g(q_n), \quad (69)$$

the sign being positive or negative according as the number of permutations is even or odd. As already seen (page 57), no two particles can have the same elementary wave functions if the complete solution is to be antisymmetric, so that there can be only one of the n_i particles associated with each of the g_i elementary eigenfunctions in any particular group. The number of complete eigenfunctions as given by Eq. (69), representing the total number of eigenstates or energy levels for the whole system, is thus equal to the number of ways in which the n particles can be distributed among the g eigenfunctions. In any particular group of n_i indistinguishable particles and g_i elementary eigenfunctions the number of possible arrangements is thus

$$\frac{g_i!}{n_i!(g_i - n_i)!}, \quad (70)$$

so that for all the n particles the probability P of the postulated

distribution is given by

$$P = \text{const.} \times \frac{g_1!}{n_1!(g_1 - n_1)!} \cdot \frac{g_2!}{n_2!(g_2 - n_2)!} \cdots \frac{g_i!(g_i - n_i)!}{n_i!(g_i - n_i)!} \quad (71)$$

or

$$P = \text{const.} \times \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \quad (72)$$

where, as before, $n = \sum_i n_i$. Upon adopting the same treatment as in the previous cases, it is seen* that

$$\ln P = \sum_i [(n_i - g_i) \ln (n_i - g_i) - n_i \ln n_i + g_i \ln g_i] + \text{const.} \quad (73)$$

The condition for the most probable state is

$$\sum_i [\ln n_i - \ln (g_i - n_i)] \delta n_i = 0; \quad (74)$$

and, with the aid of Eqs. (55) and (57) and the method of undetermined multipliers, it is found that

$$n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i} + 1}, \quad (75)$$

which is the distribution equation for the Fermi-Dirac statistics. It is seen that in Eq. (75) the term 1 appears instead of -1 in the corresponding relationship based on Bose-Einstein statistics and zero in that obtained from classical statistics. The Fermi-Dirac equation should be applied to all fundamental particles, *viz.*, electrons, protons and neutrons, and to nuclei and atoms containing an odd number of such particles. At relatively high temperatures and not too high pressures, Eq. (75) reduces to the classical form, so that for most purposes, *i.e.*, under normal conditions, the Maxwell-Boltzmann distribution law may be used as a satisfactory approximation for particles of all types.

PARTITION FUNCTIONS²

Definition of Partition Functions.—Since the probability that any molecule or atom shall have energy ϵ in any quantum state

* In the application of Stirling's theorem, it is assumed that $g_i - n_i$ is large in comparison with unity.

² See Ref. 1; also, W. H. Rodebush, *Chem. Rev.*, **9**, 319 (1931); R. H. Fowler and T. E. Sterne, *Rev. Mod. Phys.*, **4**, 635 (1932); S. Glasstone, *Ann. Rep. Chem. Soc.*, **32**, 66 (1935); L. S. Kassel, *Chem. Rev.*, **18**, 277 (1936).

that is g -fold degenerate is proportional to the quantity $g e^{-\epsilon/kT}$, the total probability of the occurrence of a particular atomic or molecular species, *i.e.*, the number of that species in a given volume, is proportional to the sum of the $g e^{-\epsilon/kT}$ terms, there being an appropriate term for every type of energy. The sum, defined by

$$f \equiv \sum_i g_i e^{-\epsilon_i/kT}, \quad (76)$$

is called the "partition function" of the atom or molecule concerned for the given volume.* The great importance of partition functions lies in the fact that from them all thermodynamic quantities such as equilibrium constants, free energies and entropies can be obtained; the principles used in deriving partition functions will be considered before their application is discussed.

Determination of Partition Functions.—The complete partition function for any species may include terms for nuclear, electronic, vibrational, rotational and translational energy, the values of which, except the last, can be obtained from spectroscopic data. For atoms and monatomic molecules the vibrational and rotational energies are zero, and so the corresponding partition functions are merely unity. For diatomic and more complex molecules, however, especially at elevated temperatures, the number of possible energy levels is extremely high, and the summation requisite for the evaluation of the partition function is very tedious. A number of approximation methods have therefore been introduced which give results in satisfactory agreement with those derived by the longer procedure, provided that the temperature is not too low: only for hydrogen and deuterium, at temperatures below 250 and 150°K., respectively, are the approximations appreciably in error.

If it is assumed that the different forms of energy distribution are independent of each other, then the complete partition function may be taken as equal to the product of the functions for the electronic, nuclear, vibrational, rotational and translational energies separately. Suppose the total energy ϵ is the sum

* This quantity was originally called the *Zustandsumme*, translated as the "state sum" or "sum over states"; the term "partition function" is now more commonly employed.

of the various energies, which are assumed not to interact; then using a numeral, *viz.*, 1, 2, 3, . . . , n , to represent the type of energy level and a letter, *viz.*, $a, b, c, \dots z$ to indicate the number of levels of each type, it follows that

$$\sum e^{-\epsilon/kT} = \sum_{a,b,c,\dots,z} e^{-(\epsilon_{1a} + \epsilon_{2b} + \epsilon_{3c} + \dots + \epsilon_{nz})/kT} \quad (77)$$

$$= \sum_a e^{-\epsilon_{1a}/kT} \sum_b e^{-\epsilon_{2b}/kT} \sum_c e^{-\epsilon_{3c}/kT} \dots \sum_z e^{-\epsilon_{nz}/kT}. \quad (77a)$$

Since the individual partition functions are of the form $\sum_i e^{-\epsilon_i/kT}$, it is evident that

$$f = f_1 f_2 f_3 \dots f_n, \quad (78)$$

where f is the complete partition function. It must be emphasized that Eq. (78) is only an approximation, since a change in vibrational energy leads to an alteration in the spacing of the rotational levels, and similarly vibrational and rotational levels are both affected by the electronic state of the molecule; however, the deviations are not serious, and Eq. (78) may be regarded as satisfactory for present purposes. The evaluation of the separate partition functions, for various forms of energy, will now be considered.

Translational Energy.—The partition function for translational energy is

$$f_{tr} = \sum g_{tr} e^{-\epsilon_{tr}/kT}; \quad (79)$$

but, as mentioned above, the levels are so closely spaced that the distribution of energy may be regarded as continuous instead of being quantized. For this reason, it is possible to replace summation by integration, the term dn , the number of levels in the energy range $d\epsilon_{tr}$, replacing g_{tr} (*cf.* page 160); thus,

$$f_{tr} = \int_0^\infty e^{-\epsilon_{tr}/kT} dn, \quad (80)$$

the integration being carried over all levels from zero to infinity. The energy of translation, for one degree of freedom, for a particle in a box of side a , *i.e.*, at constant volume, is given by Eq. (9),

thus,

$$\epsilon_{\text{tr.}} = \frac{n^2 h^2}{8a^2 m}, \quad (81)$$

so that

$$\frac{\epsilon_{\text{tr.}}}{kT} = \frac{n^2 h^2}{8a^2 m kT} \equiv n^2 \lambda, \quad (82)$$

where λ is written for the constant portion $h^2/8a^2 m kT$. Upon inserting the value of $\epsilon_{\text{tr.}}/kT$ in Eq. (80), it follows that the translational partition function for one degree of freedom is

$$f_{\text{tr.}(1)} = \int_0^\infty -n^2 \lambda \, dn = \frac{1}{2} \sqrt{\frac{\pi}{\lambda}} \quad (83)$$

$$= \frac{(2\pi m kT)^{1/2}}{a}. \quad (84)$$

Similar equations, for motion parallel to the sides b and c , can be derived for the other two degrees of freedom, so that the complete partition function for the three degrees of translational energy is the product of the three terms; *i.e.*,

$$f_{\text{tr.}} = \frac{(2\pi m kT)^{3/2}}{h^3} v, \quad (85)$$

where $v = abc$ is the volume of the box or container. The result is the translational partition function of a single molecule occupying a volume v .

Atoms and Monatomic Molecules.—For species consisting of one atom, it is necessary to consider only electronic and nuclear partition functions. The statistical weight g of each electronic energy level is $2j_s + 1$, where j_s , which has only positive values given by $l \pm s$, results from the combination of the azimuthal quantum number l and the resultant spin s of the electrons. For every value of j_s , there are $2j_s + 1$ possible orientations of similar energy in a magnetic field; if j_s is equal to $\frac{1}{2}$, for example, then $g = 2$, and there are 2 orientations, corresponding to m (magnetic quantum number) values of $\frac{1}{2}$, $-\frac{1}{2}$, 0 , $-\frac{1}{2}$, $-\frac{3}{2}$, $-\frac{5}{2}$. To obtain the complete electronic partition function the value of g must be multiplied by the appropriate $e^{-\epsilon/kT}$ term, ϵ being the electronic energy in excess of the ground state, and the results summed over all possible electronic configurations,

as indicated by spectroscopic data. The situation is simplified by the fact that the quantity $e^{-\epsilon/kT}$ has an appreciable value only when the temperature exceeds $hc\bar{\nu}/4k$, where $\bar{\nu}$ cm.⁻¹ represents the frequency separation between the given excited level and the ground state.* At ordinary temperatures the contributions of the higher energy levels are negligible provided that $\bar{\nu}$ is greater than about 1,000 cm.⁻¹; *i.e.*, the energy difference exceeds 0.125 electron-volt (e.v.). At 1000°K., however, it is permissible to ignore only those levels for which $\bar{\nu}$ exceeds 3,000 cm.⁻¹; *i.e.*, the energy difference is greater than 0.375 e.v.

The nuclear spin degeneracy of an atom or monatomic molecule is equal to $2i + 1$, where i is the number of units of nuclear spin momentum; this quantity represents the total number of possible orientations, of almost equal energy, that may be taken up by the nucleus in a perturbing field. The exponential factor involving the energy is equal to unity for the ground state, since $\epsilon_{\text{nuc.}}$ is zero, and hence $e^{-\epsilon/kT}$ is 1. The nuclear spin contribution of an atom or of a monatomic molecule to the complete partition function is thus equal to $2i + 1$.

A few examples may be given to illustrate the rules developed above. For the electronic ground state of atomic hydrogen, $l = 0$ and $s = \frac{1}{2}$, so that j_s is $\frac{1}{2}$ and $2j_s + 1$ is equal to 2; the contribution of this level to the partition function is thus 2, since the exponential term is unity. The frequency separations of the excited levels are so high that these levels can be neglected except at extremely high temperatures. The nuclear spin of hydrogen is $\frac{1}{2}$ unit, and so the spin contribution to the function is 2; the contribution of nuclear and electronic functions thus gives a partition function of 4 for atomic hydrogen. Since the deuterium atom has a spin of unity, the corresponding partition function is 6.

From spectroscopic studies it is known that the chlorine atom in the ground state is an inverted 2P doublet, the constituent terms being $^2P_{3/2}$ and $^2P_{1/2}$; the j_s values are thus $\frac{3}{2}$ and $\frac{1}{2}$ for lower and upper levels, respectively. The $2j_s + 1$, for the two levels, are 4 and 2, respectively, so that the electronic partition function is $4 + 2e^{-551hc/kT}$. No excited level need be considered at any reasonable temperature. The spin of the chlorine atom is $\frac{3}{2}$, so

* By the quantum theory the energy equivalent of radiation of frequency $\bar{\nu}$ cm.⁻¹ is equal to $hc\bar{\nu}$, where c is the velocity of light.

that the electronic contribution must be multiplied by 6 to give the combined electronic and nuclear partition function.

Diatomic Molecules.—The energy of the excited state of a molecule is generally so much in excess of the ground level that the contributions to the partition functions of all but the latter may be neglected at temperatures below 1000°K. Most diatomic molecules have $^1\Sigma$ ground terms and so exist in singlet states; a few such molecules, however, have multiplet ground states for which allowance must be made. Instances of this behavior are found with nitric oxide, oxygen and the OH radical; the appropriate allowances in these instances, together with the nuclear spin factors, are most conveniently considered in connection with the treatment of the rotational partition function.

Vibrational Partition Function.—The energy separations of successive vibrational levels are smaller than for electronic levels; therefore, it is always necessary to include a number of these levels in the sum of terms making up the partition function. Unless it happens to be degenerate, as is sometimes the case, the statistical weight of a vibrational level is unity, and so it is possible to write for the partition function

$$f_{\text{vib.}} = \sum e^{-\epsilon_{\text{vib.}}/kT}, \quad (86)$$

where $\epsilon_{\text{vib.}}$ is the difference between the vibrational energy in any level and that of the lowest level. It has been derived from quantum mechanics that for a diatomic molecule, on the assumption that it is a harmonic oscillator, the actual vibrational energy is given by

$$\epsilon_v = hc(v + \tfrac{1}{2})\omega, \quad (87)$$

where h and c have their usual significance, ω is the fundamental vibration frequency of the molecule in its ground state, expressed in wave numbers (cm.^{-1}), and v is the vibrational quantum number which may have any integral value, including zero. In the lowest level, *i.e.*, when v is zero, the zero-point vibrational energy ϵ_0 is given by

$$\epsilon_0 = \tfrac{1}{2}hc\omega, \quad (88)$$

so that $\epsilon_{\text{vib.}}$, which is defined as $\epsilon_v - \epsilon_0$, is given by

$$\epsilon_{\text{vib.}} = \epsilon_v - \epsilon_0 = hc v \omega, \quad (89)$$

where v may be any integer from zero to infinity. It follows, therefore, that the vibrational partition function is

$$f_{\text{vib.}} = \sum_{v=0}^{\infty} e^{-hcv\omega/kT} \quad (90)$$

$$= (1 - e^{-hc\omega/kT})^{-1}. \quad (91)$$

Strictly speaking this result is applicable only if the diatomic molecule behaves as a harmonic oscillator; and although spectroscopic measurements show that this condition is not satisfied in practice, nevertheless the results given by Eq. (91), especially at appreciable temperatures, differ little from those derived from band spectra.

The calculation of the vibrational partition function of a polyatomic molecule is a much more complicated process, and it is the practice to assume that the energy levels for each mode of vibration can be expressed by means of a formula of the same type as for a diatomic molecule, *i.e.*, by Eq. (87). In general, a molecule containing n atoms has $3n - 6$ normal modes of vibration. For a linear molecule, this is increased to $3n - 5$, and it is decreased to $3n - 7$ for a molecule of the type having one degree of freedom of unhindered internal rotation. Of the total, $n - 1$ are stretching, or valence, vibrations and the remainder are bending, or deformation, vibrations. If a molecule has $3n - x$ vibrational modes, then the vibrational part of the partition function may be written

$$f_{\text{vib.}} = \prod_{i=1}^{3n-x} (1 - e^{-hc\omega_i/kT})^{-1}, \quad (92)$$

or

$$f_{\text{vib.}} = \prod_{i=1}^{3n-x} (1 - e^{-h\nu_i/kT})^{-1}, \quad (92a)$$

the product being taken over all the modes; ω_i cm.⁻¹ is the fundamental frequency of the i th vibrational mode in wave numbers, and ν_i is the corresponding value in sec⁻¹.

Rotational Partition Functions.—The exact determination of the rotational partition function of even a simple molecule involves a number of complications, but it will be shown that for many purposes an approximate treatment gives results of

sufficient accuracy. The statistical weight of each rotational level is determined by both the rotational quantum numbers and the spins of the nuclei constituting the molecule. For each level of quantum number J , there are $2J + 1$ possible orientations of similar energy for a diatomic molecule, so that $2J + 1$ is the purely rotational degeneracy. This number must, however, be multiplied by the spin factor, and that depends on the nature of the molecule. If the spin of each nucleus in a homonuclear diatomic molecule is i , there are $2i + 1$ ways in which the two spins may combine, giving a series of possible values for the resultant spin of $2i, 2i - 1, 2i - 2, \dots, 2, 1, 0$. Of these the first, third, fifth, etc., correspond to symmetrical spin eigenfunctions, and the second, fourth, sixth, etc., to antisymmetrical eigenfunctions. In general, the resultant spin for the molecule (t) may be written as $2i - n$, where n is zero or an integer not exceeding $2i$; for symmetrical, *i.e.*, ortho-, states, n is even, or zero, and for antisymmetrical, *i.e.*, para-, states, n is odd. Since there are $2t + 1$ possible orientations of the molecule for every value of the spin, each resultant molecular spin is $(2t + 1)$ -fold degenerate; as t is equal to $2i - n$, the degeneracy corresponding to each combination of the two nuclear spins is $2(2i - n) + 1$. The total degeneracy of the ortho-states, *i.e.*, when n is even, is thus

$$g_{\text{nuc. (ortho)}} = \sum_{n=0,2,4,\dots,2i}^{\infty} [2(2i - n) + 1] = (i + 1)(2i + 1); \quad (93)$$

for the para-states, it is

$$g_{\text{nuc. (para)}} = \sum_{n=1,3,5,\dots,2i-1}^{\infty} [2(2i - n) + 1] = i(2i + 1). \quad (94)$$

The statistical weights due to nuclear spins are thus obtained by multiplying the ortho rotational levels by $(i + 1)(2i + 1)$ and the para-levels by $i(2i + 1)$.

The nuclear spin of the hydrogen atom is $\frac{1}{2}$ unit, so that the nuclear spin factor is 3 for the ortho-states and 1 for the para-states; from various theoretical and practical studies, it is known that in molecular hydrogen the para-levels are those for which the rotational quantum number J is even, whereas the odd values of J give the ortho-states. It follows, therefore,

that the complete rotational partition function for molecular hydrogen is

$$f_{\text{rot.}} = \sum_{J=0,2,4}^{\infty} (2J+1) e^{-\epsilon_J/kT} + 3 \sum_{J=1,3,5}^{\infty} (2J+1) e^{-\epsilon_J/kT}, \quad (95)$$

where ϵ_J is the rotational energy of the J th level.

Since the deuterium nucleus consists of two elementary particles, *viz.*, a proton and a neutron, whereas that of hydrogen is a proton only, it is evident, from what has been stated above, that the former nucleus will obey the Bose-Einstein statistics; *i.e.*, the total eigenfunction is symmetrical. But the latter will satisfy the Fermi-Dirac statistics; *i.e.*, the total eigenfunction is antisymmetrical. Since other essential properties of the two nuclei are identical, the distribution of ortho- and para-states among the rotational levels of the deuterium molecule will be opposite to that for hydrogen; *i.e.*, the even rotational levels of molecular deuterium are ortho-states, and odd values of J give the para-states. The nuclear spin of deuterium is unity, so that the spin factors are 6 and 3 for ortho- and para-states, respectively. The complete rotational partition function for molecular deuterium is thus

$$f_{\text{rot.}} = 6 \sum_{J=0,2}^{\infty} (2J+1) e^{-\epsilon_J/kT} + 3 \sum_{J=1,3,5}^{\infty} (2J+1) e^{-\epsilon_J/kT}. \quad (96)$$

For a heteronuclear molecule there are no ortho- and para-states. If i and i' are the spins of the two nuclei, the nuclear spin factor for the diatomic molecule in *all* rotational levels is

$$(2i+1)(2i'+1);$$

if i' is replaced by i , this is the same as the sum of the values for ortho- and para-states. The rotational partition function of a heteronuclear diatomic molecule is thus

$$f_{\text{rot.}} = (2i+1)(2i'+1) \sum_{J=0}^{\infty} (2J+1) e^{-\epsilon_J/kT}, \quad (97)$$

the sum being taken over all integral values of J from zero to infinity.

It was postulated above that the vibrational and rotational energies are independent. It may be assumed, therefore, as an

approximation, that the molecule is rigid; for a diatomic molecule of this type the rotational energy, as derived by quantum mechanics, is expressed by

$$\epsilon_J = \frac{J(J+1)\hbar^2}{8\pi^2 I}, \quad (98)$$

where I is the moment of inertia of the molecule. For a heteronuclear molecule, therefore, combination of Eqs. (97) and (98) gives

$$f_{\text{rot.}} = g_{\text{nuc.}} \sum_{J=0}^{\infty} (2J+1) e^{-\rho J(J+1)}. \quad (99)$$

where ρ is written for the quantity $\hbar^2/8\pi^2 I kT$ and $g_{\text{nuc.}}$ is the nuclear spin degeneracy, *i.e.*, $(2i+1)(2i'+1)$. If ρ is small, *i.e.*, at relatively high temperatures, especially for molecules having large moments of inertia, the summation in Eq. (99) may be replaced by integration; hence,

$$f_{\text{rot.}} = g_{\text{nuc.}} \int_0^{\infty} 2(J + \frac{1}{2}) e^{-(J+\frac{1}{2})^2 \rho} dJ \quad (100)$$

$$= \frac{g_{\text{nuc.}}}{\rho}, \quad (101)$$

$$\therefore f_{\text{rot.}} = g_{\text{nuc.}} \left(\frac{8\pi^2 I kT}{\hbar^2} \right). \quad (102)$$

If the diatomic molecule is homonuclear, the rotational partition function may be written, in the general case, as

$$f_{\text{rot.}} = g_{\text{nuc.}} \sum_{J=0,2,\dots}^{\infty} (2J+1) e^{-\rho J(J+1)} + g'_{\text{nuc.}} \sum_{J=1,3,\dots}^{\infty} (2J+1) e^{-\rho J(J+1)}, \quad (103)$$

where $g'_{\text{nuc.}}$ and $g''_{\text{nuc.}}$ represent the spin factor, *i.e.*, $i(2i+1)$ and $(i+1)(2i+1)$, the choice depending on the distribution of rotational levels among the ortho- and para-states. When ρ is small, the two sums in Eq. (103) become almost identical; and, upon replacing summation by integration, each is readily shown to be equal to $1/2\rho$, so that

$$f_{\text{rot.}} = \frac{g'_{\text{nuc.}} + g''_{\text{nuc.}}}{2\rho}, \quad (104)$$

where $g'_{\text{nuc.}} + g''_{\text{nuc.}}$ is $(2i + 1)^2$. This result is sufficiently accurate for all diatomic molecules, except hydrogen and deuterium, down to quite low temperatures; with the aforementioned substances, however, the moments of inertia are so relatively small that it is only above 273 and 200°K., respectively, that the approximations made do not lead to appreciable errors. This conclusion may be put in another form by saying that Eq. (104) is applicable only to hydrogen and deuterium when they contain the "normal" ortho-para ratio, *i.e.*, 3 to 1 and 1 to 2, respectively. With "equilibrium" hydrogen and deuterium at low temperatures the approximations cannot be made, and to obtain the rotational partition function it is necessary to carry out detailed summations according to Eqs. (95) and (96), the rotational energies being obtained from spectroscopic measurements.

For a homonuclear diatomic molecule having a nuclear spin of zero, such as the oxygen molecule in which both atoms are O^{16} , the nuclear spin factor for para-states, *i.e.*, $i(2i + 1)$, should be zero; this is in agreement with the observation that in the spectra of such molecules alternative rotational levels are missing. Suppose the odd values of J give the ortho-levels, which actually do appear; then the rotational partition function is

$$f_{\text{rot.}} = g_{\text{nuc.}} \sum_{J=1,3,5,\dots}^{\infty} (2J + 1) e^{-\epsilon_J/kT}. \quad (105)$$

where $g_{\text{nuc.}}$, equal to $(i + 1)(2i + 1)$, is unity since i is zero. Upon inserting the value of ϵ_J from Eq. (98) and making the assumption, as before, that ρ is small, it is seen, after replacing summation by integration, that Eq. (105) becomes

$$f_{\text{rot.}} = \frac{1}{2\rho}. \quad (106)$$

This would give the correct result, including the nuclear spin allowance, if the molecule had a singlet ground state, as is the case with most diatomic molecules. Oxygen, however, has a $^3\Sigma$ ground term, so that the lowest level is a triplet state. Since the energy separation of the three levels is small, their contributions to the partition function may be taken as identical; it follows, therefore, that for the oxygen molecule the rotational partition function, including electronic and nuclear factors, is

$$f_{\text{rot.}} = \frac{3}{2\rho}, \quad (107)$$

provided that the temperature does not exceed 1000°K. , at which the first excited level must be taken into consideration (page 172).

In nitric oxide, which is represented in the ground state by a $^2\Pi$ term, the doublets have a frequency separation of 120 cm.^{-1} , which is too large to be ignored; allowance must therefore be made by including the factor $e^{-hc\bar{\nu}/kT}$, where $\bar{\nu}$ is 120 cm.^{-1} . Further, molecules having other than Σ ground terms exhibit what is known as Λ -type doubling, whereby every rotational level is split into two closely spaced sub-levels; it is consequently necessary to multiply the rotational function by a factor of 2 so as to allow for this doubling. The complete rotational partition function, with electronic and nuclear contributions for nitric oxide, may therefore be written*

$$f_{\text{rot.}} = g_{\text{el.}}g_{\text{nuc.}}(1 + e^{-hc\bar{\nu}/kT}) \sum_{J=\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots}^{\infty} (2J + 1) e^{-\epsilon_J/kT}, \quad (108)$$

where $g_{\text{el.}}$ is the electronic statistical weight, which in this case is 2 for the Λ -type doubling; and $g_{\text{nuc.}}$ is equal to 3, since the nuclear spins N^{14} and O^{16} are 1 and 0, respectively. The quantity 1 in the first parentheses is the exponential energy factor, with $\epsilon = 0$, for the lower multiplet of the ground level, and the other term is that for the higher level, with $\bar{\nu} = 120\text{ cm.}^{-1}$ as explained above. The summation factor may be evaluated as in the previous cases by the method of integration; the result is found to be the same as in Eq. (102).

Summarizing the results of the treatment of the individual substances, it is evident that the combined electronic, nuclear and rotational contributions to the partition function of any diatomic molecule may be represented by

$$f_{\text{rot.}} = \frac{g_{\text{el.}}g_{\text{nuc.}}}{\sigma} \cdot \frac{(8\pi^2 I k T)}{h^2}, \quad (109)$$

where $g_{\text{nuc.}}$ is $(2i + 1)(2i' + 1)$, whether i and i' are the same or different; and σ is called the "symmetry number." The symmetry number represents the number of indistinguishable

* The equation given is not exact, for the two levels of the doublet do not have the same J values and the summations are not identical; at appreciable temperatures, however, the difference is negligible. It should be remarked, further, that for nitric oxide the J values are not integral but are half the odd integers, *viz.*, $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, etc.

orientations of the particular molecule as a result of rotation. For homonuclear diatomic substances, *e.g.*, H_2 , D_2 , O_2 and N_2 , σ is equal to 2; for heteronuclear molecules, it is unity. It should be noted that molecules in which the two atoms differ isotopically, *e.g.*, HD , $\text{O}^{16}\text{O}^{18}$, $\text{N}^{14}\text{N}^{15}$, $\text{Cl}^{35}\text{Cl}^{37}$, must be regarded as heteronuclear, for they do not have ortho- and para-states. The electronic and nuclear spin factors $g_{\text{el.}}$ and $g_{\text{nuc.}}$ must, of course, be considered separately for every case.

Polyatomic Molecules.—Equation (109) may be employed for the rotational partition function of any rigid, *linear*, polyatomic molecule, for such molecules have one moment of inertia only; the symmetry number is unity for unsymmetrical substances, *e.g.*, HCN and N_2O , but it is 2 for CO_2 and C_2H_2 . The nuclear contribution is always given by the product of the $2i + 1$ terms for all the atoms in the molecule.

The rotational partition function for a rigid, nonlinear, polyatomic molecule with three equal moments of inertia, *i.e.*, a rigid spherical rotator, such as methane or carbon tetrachloride, is

$$f_{\text{rot.}} = g_{\text{el.}}g_{\text{nuc.}} \sum_{J=0}^{\infty} (2J+1)^2 e^{-\rho J(J+1)}, \quad (110)$$

where ρ is defined, as before, by

$$\rho \equiv \frac{h^2}{8\pi^2 I k T}, \quad (111)$$

I being, as usual, the moment of inertia. If summation is replaced by integration, in the usual manner, it is found that

$$f_{\text{rot.}} = \frac{g_{\text{el.}}g_{\text{nuc.}}}{\sigma} \frac{1}{\rho^{3/2}} \quad (112)$$

$$= \frac{g_{\text{el.}}g_{\text{nuc.}}}{\sigma} \pi^{1/2} \left(\frac{8\pi^2 I k T}{h^2} \right)^{3/2}, \quad (113)$$

the value of σ being 12 for molecules of the type CR_4 . It should be noted that these equations are applicable only if there is no free rotation within the molecule.

If the molecule is of the symmetrical top form, *e.g.*, ammonia and chloroform, two of the three moments of inertia are equal; the expression for the rotational energy is relatively complicated,

and it is possible to derive only an approximate equation for the rotational partition function, thus,

$$f_{\text{rot.}} = \frac{g_{\text{el.}} g_{\text{nuc.}}}{\rho_A \rho_C^{1/2}} \frac{\pi^{3/2}}{\sigma} \quad (114)$$

where ρ_A and ρ_C are defined by expressions similar to Eq. (111), with the appropriate moments of inertia A , for the two which are equal, and C , for the third. It is evident that Eqs. (112) and (114) are identical in form, and hence it is apparent that for an asymmetrical top, with three different moments of inertia, *viz.*, A , B and C , the rotational partition function may be represented by the analogous equation

$$f_{\text{rot.}} = \frac{g_{\text{el.}} g_{\text{nuc.}}}{(\rho_A \rho_B \rho_C)^{1/2}} \frac{\pi^{3/2}}{\sigma} \quad (115)$$

Upon inserting the values for ρ_A , ρ_B and ρ_C , it is seen that Eq. (115) may be written in the form, in which it is often used:

$$f_{\text{rot.}} = \frac{g_{\text{el.}} g_{\text{nuc.}}}{\sigma} \frac{8\pi^2 (8\pi^3 A B C)^{1/2} (kT)^3}{h^3} \quad (116)$$

If the asymmetrical rotator is planar, as with water and benzene, there is some simplification, for $A + B$ is equal to C ; in the two instances mentioned, σ is 2 and 12, respectively.

Partition Functions and Equilibrium Constants.—If any system in a state A can pass into a state B , and vice versa, as the result of a chemical or physical transformation, then the equilibrium constant K_e of the system is given by

$$K_e = \frac{\text{concentration in final state}}{\text{concentration in initial state}} \quad (117)$$

$$= \frac{\text{no. of molecules in final state/volume of system}}{\text{no. of molecules in initial state/volume of system}} \quad (118)$$

It has been seen (page 169) that the number of molecules of any kind contained in a given volume is proportional to the complete partition function of the particular species in that volume, and so Eq. (118) may be written

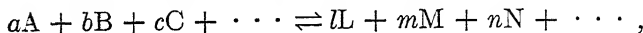
$$K_e = \frac{f_f/V}{f_i/V}, \quad (119)$$

* This equation may be regarded as the general form for $f_{\text{rot.}}$ of a non-linear molecule. If $A = B = C$, it reduces to Eq. (112); if $A = B$, it becomes (114).

where f_f and f_i are the partition functions of final and initial states, respectively, and V is the volume of the system. Since the f terms include the translational partition function, which according to Eq. (85) is proportional to the volume of the system, it follows that

$$K_c = \frac{F_f}{F_i}, \quad (120)$$

where the F terms are the partition functions for *unit volume*; in other words, in deriving the F functions the volume term is omitted. By using exactly similar arguments to those given above, it can be readily shown that, for the reversible reaction



the equilibrium constant may be written in terms of the partition functions, per unit volume, of the respective species; thus,

$$K_c = \frac{F_L^l F_M^m F_N^n}{F_A^a F_B^b F_C^c} \quad (121)$$

It is evident, therefore, that if the partition functions are known the equilibrium constant of the system can be determined; and hence the free-energy change for the reaction and other thermodynamic quantities may be derived without difficulty.

Since the equilibrium constant is a ratio of partition functions, in which the energy appears in exponential terms, thus,

$$K_c = \frac{F_f}{F_i} = \frac{\sum_f g_f e^{-\epsilon_f/kT}}{\sum_i g_i e^{-\epsilon_i/kT}}, \quad (122)$$

it is evident that any arbitrary energy level may be chosen as the zero from which the energies of the various levels ϵ_i and ϵ_f are estimated. For example, suppose the energy curve for any change is as represented in Fig. 52, in which the various quantum levels for a particular type of energy are indicated by horizontal lines. The lowest (zero-level) quantum level of the initial state, *i.e.*, at the absolute zero, may be taken as the arbitrary zero of reference; all energies ϵ_i for the initial state and ϵ_f for the final state should then be reckoned from this level in calculating the partition function. Alternatively, ϵ_f' may be taken

as the sum of ϵ_0 and ϵ_f , the former being the difference in the zero-level energies of initial and final states and the latter being the energy of any level in the final state with reference to its own zero-level; thus,

$$\epsilon'_f = \epsilon_0 + \epsilon_f,$$

and so it follows that

$$F_f = \sum_f g_f e^{-\epsilon'_f/kT} = e^{-\epsilon_0/kT} \sum_f g_f e^{-\epsilon_f/kT}. \quad (123)$$

It is the final form of this relationship that is frequently employed, especially in connection with the problem of reaction rates.

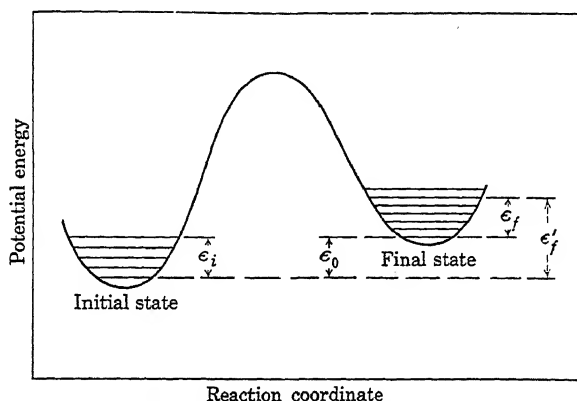
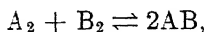


FIG. 52.—Energy levels for calculation of partition functions.

It should be noted that although Fig. 52 is employed to represent one type of energy the general arguments apply to all forms of energy; it is only with vibrational energy, however, that there is any appreciable amount of zero-point energy. The quantity ϵ_0 may therefore be regarded as the difference in total energy of final and initial states at the absolute zero.

It has been seen that the complete partition function should include the nuclear spin factors of the various species; but in most calculations of equilibrium constants these factors may be omitted, as may be shown in the following manner. Consider the simple reaction



for which the equilibrium constant is given by

$$K = \frac{F_{AB}^2}{F_A \times F_B}, \quad (124)$$

where F_A , F_B and F_{AB} are the partition functions for unit volume of the molecules A_2 , B_2 and AB , respectively. Let Q_A , Q_B and Q_{AB} represent the corresponding partition functions, excluding the nuclear spin effect; the complete partition functions including this factor are then

$$F_A = \frac{1}{2}Q_A(2i_A + 1)^2, \quad F_B = \frac{1}{2}Q_B(2i_B + 1)^2, \\ F_{AB} = Q_{AB}(2i_A + 1)(2i_B + 1),$$

where i_A and i_B are the nuclear spins of the atoms A and B. The equilibrium constant, according to Eq. (124), is then

$$K = \frac{[Q_{AB}(2i_A + 1)(2i_B + 1)]^2}{[\frac{1}{2}Q_A(2i_A + 1)^2][\frac{1}{2}Q_B(2i_B + 1)^2]} = \frac{4Q_{AB}^2}{Q_A Q_B}. \quad (125)$$

If the terms containing the nuclear spins i_A and i_B had been completely disregarded, but the symmetry number, which is 2 for both A_2 and B_2 and unity for AB , introduced, the partition functions would have been $\frac{1}{2}Q_A$, $\frac{1}{2}Q_B$ and Q_{AB} , respectively. Employing these in Eq. (124), in place of the F functions, gives

$$K = \frac{Q_{AB}^2}{(\frac{1}{2}Q_A)(\frac{1}{2}Q_B)} = \frac{4Q_{AB}^2}{Q_A Q_B}, \quad (126)$$

which is identical with Eq. (125). The equilibrium constant obtained by the use of partition functions in which nuclear spin terms have been omitted, but symmetry factors included, is thus correct, and the same conclusion can be reached by considering any reaction; it is immaterial whether symmetrical or unsymmetrical molecules or even atoms are involved. The only exceptions to this rule are cases in which there is a change in the ortho-para ratio during the course of the reaction; in these circumstances the approximate equation (104), and those related to it, cannot be used, and the more complicated summation procedure must be adopted instead.

THE THEORY OF ABSOLUTE REACTION RATES

Statistical Calculation of Reaction Rates.³—The particular application of partition functions that has been the object of

³ H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935); *Chem. Rev.*, **17**, 65 (1935); *Trans. Faraday Soc.*, **34**, 41 (1938); for earliest applications of statistical methods to the study of reaction rates, see references on p. 11.

this chapter is that involved in the statistical calculation of reaction velocities. In any atomic or molecular process requiring an activation energy, *i.e.*, one in which the rate is dependent on a factor of the type $e^{-\alpha/T}$, the atoms or molecules involved must first come together to form an activated complex, or, in general, an "activated state" must be formed. As seen in Chap. III, the complex is regarded as being situated at the top of an energy barrier lying between the initial and final states, and the rate of reaction is given by the velocity at which the activated complex travels over the top of the barrier. It has been shown that the configuration corresponding to the activated state has all the properties of an ordinary molecule, except that the normal vibration frequency in the coordinate of decomposition has an imaginary value: *i.e.*, the activated complex is stable for atomic displacements in all directions but one, and in the latter it falls to pieces. If the energy barrier in the vicinity of the activated state is relatively flat, then the degree of freedom in the decomposition coordinate may be considered statistically as a one-dimensional translation. In this way, the $3n$ degrees of freedom of the activated complex are retained, n being the number of atoms it contains.*

For the statistical treatment of reaction rates, it will be supposed that *the initial reactants are always in equilibrium with the activated complexes*† and that the latter decompose at a definite rate. It is convenient arbitrarily to define an activated state, and for this purpose it may be imagined to exist at the top of the energy barrier in a potential box of length δ (Fig. 53); as will be seen shortly, the actual magnitude is immaterial, since it cancels out in the final expression.

The net rate at which the reaction occurs is determined by the average velocity of the activated complexes over the top of the barrier. It was shown on page 161 that the probability

* In order to specify a single activated complex in quantum mechanics, it is necessary to postulate a region of appreciable size at the top of the barrier on account of the uncertainty principle. In classical theory, there is no such restriction, and for most chemical reactions the flatness of the barrier makes the restriction unimportant. The consideration of the statistical average of many complexes, as is undertaken below, has a similar effect.

† This is one of the fundamental postulates of the theory developed here; it is supposed that the reaction does not appreciably disturb the equilibrium concentration of activated complexes.

$P(\dot{x})_1$ of a molecule having a velocity between \dot{x} and $\dot{x} + d\dot{x}$ in one degree of freedom is

$$P(\dot{x})_1 = \text{const.} \times e^{-\frac{1}{2}m\dot{x}^2/kT} d\dot{x}, \quad (127)$$

where γ of Eq. (40) has been replaced by its equivalent value kT . On the assumption that there is an equilibrium distribution of velocities in the activated state, the average velocity of

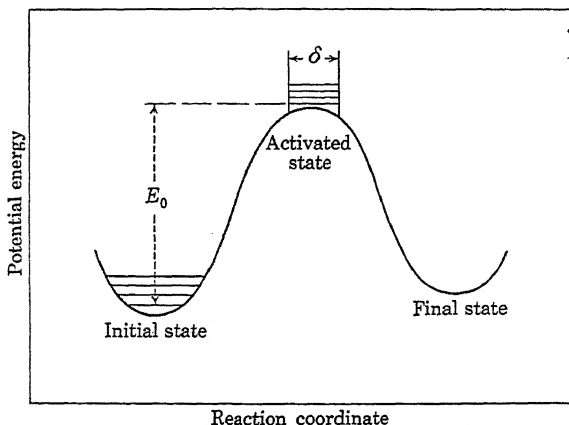


FIG. 53.—Potential-energy curve for reaction showing imaginary potential box containing the activated state.

the complexes in one direction, *e.g.*, in the forward direction, is then

$$\bar{\dot{x}} = \frac{\int_0^{\infty} e^{-\frac{1}{2}m\dot{x}^2/kT} \dot{x} d\dot{x}}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}m\dot{x}^2/kT} d\dot{x}}, \quad (128)$$

where the limits of integration in the denominator are taken from ∞ to $-\infty$ to allow for the fact that the complexes are moving in both directions, whereas in the numerator the limits are zero to infinity because it is the mean velocity in the direction of decomposition that is required. Evaluation of the standard integrals gives

$$\bar{\dot{x}} = \left(\frac{kT}{2\pi m} \right)^{\frac{1}{2}}, \quad (129)$$

so that the average rate of passage of activated complexes over the barrier in one direction along the coordinate of decomposition

is $(kT/2\pi m^*)^{1/2}$, where m^* is the effective mass of the complex in the same direction.

The average time τ of crossing the barrier, which is the mean life of an activated complex, is equal to the length δ of the top of the barrier divided by the average rate of crossing \bar{x} as given by Eq. (129): thus,

$$\tau = \frac{\delta}{\bar{x}} = \delta \left(\frac{2\pi m^*}{kT} \right)^{1/2} \quad (130)$$

The fraction of the activated complexes crossing the barrier in unit time is equal to $1/\tau$; and hence if c_{\ddagger} is the number of activated complexes per unit volume lying in the length δ of the coordinate of decomposition, the quantity c_{\ddagger}/τ gives the number of complexes crossing the barrier per unit volume in unit time. If every complex that moves across the barrier falls to pieces, *i.e.*, if the transmission coefficient (page 146) is unity, c_{\ddagger}/τ is equal to the reaction velocity; *i.e.*,

$$\text{Rate of reaction} = \frac{c_{\ddagger}}{\tau} = c_{\ddagger} \left(\frac{kT}{2\pi m^*} \right)^{1/2} \frac{1}{\delta} \quad (131)$$

If the species A, B, . . . , etc., are reacting together to form the activated complex and k is the specific reaction rate using concentration units, the actual velocity, *i.e.*, the number of molecules decomposing per unit volume in unit time, is $kc_A c_B \dots$ where c_A, c_B, \dots , are the concentrations, in molecules per unit volume, of A, B, It follows, therefore, that

$$\text{Rate of reaction} \equiv kc_A c_B \dots = c_{\ddagger} \left(\frac{kT}{2\pi m^*} \right)^{1/2} \frac{1}{\delta} \quad (132)$$

and hence,

$$k = \frac{c_{\ddagger}}{c_A c_B \dots} \left(\frac{kT}{2\pi m^*} \right)^{1/2} \frac{1}{\delta} \quad (133)$$

Since it has been postulated that the activated complex is in equilibrium with the reactants, it is possible to write the equilibrium constant for the system as

$$K_c = \frac{a_{\ddagger}}{a_A a_B \dots} \quad (134)$$

where the a terms are the activities of the various species. If the substances involved may be regarded as behaving ideally, the activities can be replaced by concentrations so that

$$K_c = \frac{c_{\ddagger}}{c_A c_B \dots} \quad (135)$$

An alternative method of expressing the equilibrium constant is to employ partition functions, as seen on page 181; thus,

$$K_c = \frac{F_{\ddagger}'}{F_A F_B \dots} \quad (136)$$

where the F terms are the complete partition functions for unit volume. By following the device of Eq. (123) and taking the difference in the zero-level energies out of the partition functions, Eq. (136) becomes

$$K_c = \frac{F_{\ddagger}'}{F_A F_B} e^{-E_0/RT} \quad (137)$$

where E_0 is the difference between the zero-level energy *per mole*† of activated complex and that of the reactants (see Fig. 18). This quantity is the amount of energy that the reactants must acquire, at 0°K., before they can become activated and react; *i.e.*, E_0 is the energy of activation of the reaction at 0°K. (*cf.* page 98). It will be seen that since E_0 is the energy difference per mole, the Boltzmann constant k has been replaced by R , the gas constant per mole. Now that the $e^{-E_0/RT}$ factor has been eliminated from the partition functions, it must be remembered that in the evaluation of the F terms in Eq. (137) the energy zero is to be taken as the zero-level energy of the respective species *in each case*; this coincides, in fact, with the usual method of expressing partition functions and so introduces no complicating factor. By combining Eqs. (133), (135) and (137), it is seen that

$$k = \frac{F_{\ddagger}'}{F_A F_B \dots} \left(\frac{kT}{2\pi m^*} \right)^{1/2} \frac{1}{\delta} e^{-E_0/RT} \quad (138)$$

† The convention adopted here and, as far as possible, throughout this book is to use an italic capital E for energy *per mole* and the Greek letter ϵ for energy *per molecule*.

It is convenient to use instead of F_{\ddagger}' , which is the complete partition function for the activated complex, a new function F_{\ddagger} which does not include the contribution $f_{\text{tr.}(1)}^{\ddagger}$ due to translational motion in the one degree of freedom along the coordinate of decomposition, *i.e.*, $F_{\ddagger}' = F_{\ddagger} f_{\text{tr.}(1)}^{\ddagger}$. The translational partition function $f_{\text{tr.}(1)}^{\ddagger}$ is given by Eq. (84) as

$$f_{\text{tr.}(1)}^{\ddagger} = \frac{(2\pi m^* kT)^{1/2}}{h} \delta, \quad (139)$$

so that Eq. (138) becomes

$$k = \frac{kT}{h} \frac{F_{\ddagger}'}{F_A F_B} e^{-E_0/RT}. \quad (140)$$

It should be noted that the combination of the two terms involving the properties of the activated complex along the coordinate of decomposition, *viz.*, $(2\pi m^* kT)^{1/2}/h$, the partition function, and $(kT/2\pi m^*)^{1/2}$, the velocity in the direction of decomposition, has given the quantity kT/h , which is the same for reactants and reactions of all types. It is, therefore, a universal constant, with the dimensions of a frequency, for each temperature; it represents the frequency with which any activated complex crosses the barrier at a given temperature, and its value is about 6×10^{12} at 300°K .§

In order to allow for the possibility that not every activated complex reaching the top of the barrier and moving along the

† Since the combination of Eqs. (138) and (139) results in the elimination of δ , there is obviously no restriction on its magnitude. If it had been chosen as equal to $h/(2\pi m^* kT)^{1/2}$, which is of the order of 10^{-8} cm., $f_{\text{tr.}(1)}^{\ddagger}$ would have been unity; in these circumstances, F_{\ddagger}' and F_{\ddagger} are identical, and hence it would not be necessary to include the additional degree of translational freedom along the decomposition coordinate in the former.

§ An approximate derivation of the kT/h factor from another point of view is as follows. The classical partition function, which is also the quantum-theory value at appreciable temperatures, for a vibrational mode of frequency ν is $kT/h\nu$. The rate at which decomposition occurs, *i.e.*, the rate of passage over the barrier, may be taken as equal to the frequency ν of vibration of the activated complex along the reaction coordinate, since every vibration leads to disintegration. The product of the corresponding partition function $(kT/h\nu)$ and the rate of passage over the barrier ν gives kT/h , as found above.

coordinate of decomposition leads to reaction, it is necessary to introduce the transmission coefficient κ ; then,

$$k = \kappa \frac{kT}{h} \cdot \frac{F_{\ddagger}}{F_A F_B} \quad (141)$$

If the activated complex were a normal molecule with a stiff vibration or if the value of δ were chosen, as suggested in the footnote on page 189 so as to make $f_{tr.(1)}^{\ddagger}$ equal to unity, the partition function would have just the value F_{\ddagger} that appears in Eqs. (140) and (141). It follows, therefore, that

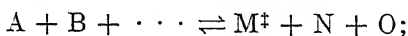
$$\left(\frac{F_{\ddagger}}{F_A F_B \cdots} \right)^{e^{-E_0/RT}}$$

may be regarded as the equilibrium constant for activated and initial states, all the molecules being treated as normal. If this equilibrium constant is represented by the symbol K^{\ddagger} , Eq. (141) reduces to the simple form

$$k = \kappa \frac{kT}{h} K^{\ddagger} \quad (142)$$

It will be recalled that Eq. (142) has been derived on the assumption that the specific reaction rate is expressed in terms of concentrations, *i.e.*, the standard state is unit concentration; under these conditions K^{\ddagger} is a concentration equilibrium constant. If pressure units had been employed instead of concentrations for the specific rate constant, *i.e.*, the standard state is unit pressure, it can be readily shown that K^{\ddagger} would be a pressure equilibrium constant. It follows, therefore, that provided that the same units are employed for k and K^{\ddagger} , Eq. (142) is of general applicability. It should be noted, however, that equations involving partition functions, *e.g.*, Eq. (141), hold only for concentration units.

In some processes the formation of the activated complex is accompanied by the liberation of other molecules or ions which take no further part in the reaction; thus, A and B, etc., may combine to yield the activated complex M^{\ddagger} , but at the same time the stable species N and O may be formed. The equilibrium between initial and activated states is thus



application of the methods used above leads to the following expression, analogous to Eq. (141),

$$k = \kappa \frac{kT}{h} \cdot \frac{F_{\ddagger} F_N F_O}{F_A F_B \cdots} e^{-E_0/RT}, \quad (143)$$

and this can be written in the form of Eq. (142), where K^\ddagger represents the equilibrium constant between A, B, etc., on the one hand and M^\ddagger , N and O on the other.

Equations (141), (142) and (143), or their equivalents, should give the specific reaction rate of any reaction, in any phase, provided that the slow process is the surmounting of an energy barrier; they constitute the basis of what has become known as the "theory of absolute reaction rates."

Leakage through Energy Barriers.⁴—According to the classical treatment the reacting molecules must surmount the energy barrier before they can pass to the state of resultants, but quantum mechanically there is a definite probability that molecules with a smaller amount of energy will succeed in getting from the initial to the final state. This effect, known as "tunneling" or "leakage" through the energy barrier, depends on the curvature of the top of the barrier, and to allow for it requires the inclusion of an additional factor $1 - \frac{1}{24}(\hbar\nu_l/kT)^2$ in Eqs. (141) and (142). The quantity ν_l is the imaginary value of the frequency of the stretching vibration along the coordinate of decomposition; it can be calculated from the potential-energy surface by the method described on page 118. Since ν_l is an imaginary quantity, ν_l^2 is negative, so that the correction term is greater than unity; the higher the temperature and the smaller the curvature of the surface, the more closely does it approach unity. The leakage effect is generally small and can usually be neglected without serious error. For a flat surface, *i.e.*, one of small curvature, the numerical value of ν_l^2 is small, and so the behavior approximates to that to be expected from classical considerations.

SPECIFIC-RATE EQUATIONS⁵

Unimolecular Reactions.—It is of interest to derive at this point some actual equations for the specific rates of simple

⁴ E. P. Wigner, *Z. physik. Chem.*, **B**, **19**, 903 (1932); *cf.* C. Eckart, *Phys. Rev.*, **35**, 1303 (1930); R. P. Bell, *Proc. Roy. Soc.*, **139**, A, 446 (1933).

⁵ Eyring, *Ref. 3*; J. O. Hirschfelder, H. Eyring and B. Topley, *J. Chem. Phys.*, **4**, 170 (1936); A. Wheeler, B. Topley and H. Eyring, *ibid.*, **4**, 178 (1936).

reactions, based on the application of Eq. (141). Consider, in the first place, a unimolecular reaction involving the decomposition of a nonlinear molecule containing n atoms. If the activated complex is treated as a normal molecule with $3n - 7$ degrees of vibrational freedom, the partition function is the product of the normal partition function for three degrees of translational freedom, for unit volume, *viz.*,

$$F_{tr.} = \frac{(2\pi mkT)^{3/2}}{h^3} \quad (144)$$

m being the *actual* mass of the activated complex,* the partition function for three degrees of rotation, as obtained from the appropriate forms of Eqs. (115) and (116), and that for the $3n - 7$ vibrational modes, *viz.*,

$$F_{vib.} = \prod_{3n-7} (1 - e^{-h\nu_{\dagger}/kT})^{-1} \quad (145)$$

The partition function for the initial state is given by the product of three similar terms, the one for translation being, in fact, identical with that for the activated state. The value of the rotational partition function is also given by Eq. (115) or (116), by use of the appropriate symmetry numbers and moments of inertia. In the vibrational partition function, there are now $3n - 6$ terms, as for any nonlinear molecule. On the assumption that the electronic factor is the same in initial and activated states, substitution in Eq. (141) gives for the specific rate constant

$$k = \kappa \frac{\sigma_i}{\sigma_{\dagger}} \left(\frac{A_{\dagger} B_{\dagger} C_{\dagger}}{A_i B_i C_i} \right)^{1/2} \frac{\prod_{3n-6} (1 - e^{-h\nu_{\dagger}/kT})^{-1}}{\prod (1 - e^{-h\nu_i/kT})^{-1}} \frac{kT}{h} e^{-E_0/RT}, \quad (146)$$

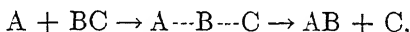
where the suffix i refers to the initial state and the symbol \dagger to the activated state. If $kT \gg h\nu$, *i.e.*, at relatively high temperatures, the vibrational degrees of freedom approach classical behavior and the $(1 - e^{-h\nu/kT})^{-1}$ terms may be replaced by $kT/h\nu$; Eq. (145) then reduces to

* This is not the same as the effective mass m^* along the decomposition coordinate which is used in Eq. (139).

$$k = \kappa \frac{\sigma_i}{\sigma_{\ddagger}} \left(\frac{A_{\ddagger} B_{\ddagger} C_{\ddagger}}{A_i B_i C_i} \right)^{\frac{1}{2}} \frac{\prod_{i=1}^{3n-6} \nu_i}{\prod_{\ddagger} \nu_{\ddagger}} e^{-E_0/RT}. \quad (146a)$$

Alternatively, if the vibration frequency is large and the temperature not too high, $e^{-h\nu/kT}$ is not greatly different from unity; the partition function for vibration is then approximately equal to unity.

Bimolecular Reactions.—For a simple bimolecular reaction involving an atom and a diatomic molecule,



the activation energy is smallest when the activated complex $A \cdots B \cdots C$ is linear, provided that s -electrons are involved (page 89), and so this configuration will be assumed. Designating properties of the reactants A and BC by means of the suffixes 1 and 2, respectively, the various partition functions are as follows:

$$F_{\ddagger} = g_{\ddagger} \frac{(2\pi m_{\ddagger} kT)^3}{h^3} \cdot \frac{8\pi^2 I_{\ddagger} kT}{\sigma_{\ddagger} h^2} \prod_{i=1}^3 (1 - e^{-h\nu_i/kT})^{-1}. \quad (147)$$

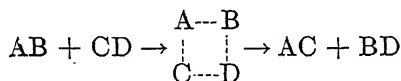
$$F_i = g_1 \frac{(2\pi m_1 kT)^{3/2}}{h^3} \cdot g_2 \frac{(2\pi m_2 kT)^{3/2}}{h^3} \cdot \frac{8\pi^2 I_2 kT}{\sigma_2 h^2} (1 - e^{-h\nu_2/kT})^{-1}. \quad (148)$$

It will be seen that the complex has three and the molecule AB only one vibrational mode; the atom A makes, of course, neither a rotational nor a vibrational contribution to the partition function. Insertion of the values of F_{\ddagger} and F_i in Eq. (141) and making appropriate cancellations give

$$k = \kappa \frac{g_{\ddagger}}{g_1 g_2} \left(\frac{m_{\ddagger}}{m_1 m_2} \right)^{3/2} \frac{I_{\ddagger} \sigma_2}{I_2 \sigma_{\ddagger}} \cdot \frac{h^2}{(2\pi)^{3/2} (kT)^{1/2}} \cdot \frac{1 - e^{-h\nu_2/kT}}{\prod (1 - e^{-h\nu_i/kT})} e^{-E_0/RT}. \quad (149)$$

Further simplification may be made, as shown above, if the vibration becomes classical, *e.g.*, at high temperature, or if ν is large and the temperature not too high.

When the bimolecular reaction is of the type



the result is somewhat more complicated. The activated complex must be treated as a nonlinear molecule with five vibrational modes. By use of the suffixes 1, 2 and ‡ for AB, CD and the complex, respectively, the partition functions are

$$F_{\ddagger} = g_{\ddagger} \frac{(2\pi m_{\ddagger} kT)^{3/2}}{h^3} \cdot \frac{8\pi^2 (8\pi^3 A_{\ddagger} B_{\ddagger} C_{\ddagger})^{1/2} (kT)^{3/2}}{\sigma_{\ddagger} h^3} \prod^5 (1 - e^{-h\nu_{\ddagger}/kT})^{-1}, \quad (150)$$

$$F_i = g_i \frac{(2\pi m_i kT)^{3/2}}{h^3} \cdot \frac{8\pi^2 I_1 kT}{\sigma_1 h^2} (1 - e^{-h\nu_1/kT})^{-1} \\ \cdot \frac{(2\pi m_2 kT)^{3/2}}{h^3} \cdot \frac{8\pi^2 I_2 kT}{\sigma_2 h^2} (1 - e^{-h\nu_2/kT})^{-1} \quad (151)$$

Insertion of these values in Eq. (141) gives the appropriate specific rate constant.

Classical and Experimental Activation Energies.—The equations of the theory of absolute reaction rates give the activation energy factor in the form $e^{-E_0/RT}$, but the activation energy derived directly from the potential-energy surfaces described in Chap. III is the so-called "classical" value E_c per mole. It is of interest, therefore, to see what modification is necessary in order that the factor $e^{-E_c/RT}$ may be employed. As seen on page 98, $E_c = E_0 - N \sum \epsilon_0$, where $\epsilon_0 = \frac{1}{2} h\nu$ per molecule represents the zero-point energy for every mode of vibration, and N is the Avogadro number. The product of the vibrational partition functions and the $e^{-E_0/RT}$ term can be rewritten in view of this relationship between E_0 and E_c , the result being

$$\prod (1 - e^{h\nu/kT})^{-1} e^{-E_0/RT} = \prod \frac{e^{-\frac{1}{2} h\nu/kT}}{(1 - e^{-h\nu/kT})} e^{-E_c/RT} \quad (152)$$

$$= \prod 2[\sinh \frac{1}{2}(h\nu/kT)]^{-1} e^{-E_c/RT}. \quad (153)$$

It is satisfactory, therefore, when writing the specific-rate equations to replace each vibrational partition function by $2[\sinh (\frac{1}{2} h\nu/kT)]^{-1}$ and at the same time E_0 by E_c .

The experimental activation energy E_{exp} per mole is obtained from the expression

$$\frac{d \ln k}{dT} = \frac{E_{\text{exp}}}{RT^2}, \quad (154)$$

and the relationship between E_{exp} and E_0 can readily be obtained by logarithmic differentiation of the theoretical expression for

the specific reaction rate. The difference between the experimental activation energy and E_0 will clearly depend on the terms involving the temperature in the numerator and denominator of the rate equation; each type of case must, therefore, be considered separately. For the bimolecular reaction between AB and CD, for example, it is found that

$$E_{\text{exp.}} = E_0 + N \left[\sum_{i=1}^5 \frac{h\nu_i^\ddagger}{e^{h\nu_i^\ddagger/kT} - 1} - \sum_{i=1}^2 \frac{h\nu_i}{e^{h\nu_i/kT} - 1} - kT \right], \quad (155)$$

where N is the Avogadro number and $E_{\text{exp.}}$ and E_0 refer to a mole of each reactant.*

THERMODYNAMICS OF REACTION RATES⁶

Free Energy of Activation.—The constant K^\ddagger for the equilibrium between the activated complex, treated as a normal molecule, and the reactants may be expressed in terms of the standard free energy of the process (ΔF^\ddagger) by means of the familiar thermodynamic equation

$$-\Delta F^\ddagger = RT \ln K^\ddagger. \quad (156)$$

The quantity ΔF^\ddagger is the *standard*† free energy of the activation process, although it is generally called the “free energy of activation.” For the present, it is unnecessary to specify the actual standard state, it being understood that it is chosen so as to agree with the units employed in expressing the specific reaction rate. If the value of K^\ddagger given by Eq. (156) is introduced into (142), it follows that

$$k = \frac{kT}{h} e^{-\Delta F^\ddagger/RT}, \quad (157)$$

the transmission coefficient being omitted for the sake of simplicity. Further, if ΔF^\ddagger is replaced by its equivalent $\Delta H^\ddagger - T \Delta S^\ddagger$,

* The inclusion of N is necessary because the specific-rate equations given above give the rates in terms of *molecules* of reactants, etc.

⁶ W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **3**, 492 (1935); see also M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935); **32**, 1333 (1936); **33**, 448 (1937); E. A. Guggenheim, *ibid.*, **33**, 607 (1937).

† The symbol \ddagger applied to a thermodynamic quantity, e.g., ΔF^\ddagger , ΔS^\ddagger , ΔH^\ddagger , etc., invariably refers to the change accompanying the activation process with *all substances in their standard states*. Since no confusion is likely to arise by the omission of the usual zero superscript, this is left out to avoid complexity of representation.

the result is

$$k = \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}, \quad (158)$$

where ΔH^\ddagger and ΔS^\ddagger are the standard heat and entropy changes, respectively, accompanying the activation process (these are frequently referred to as the "heat of activation" and "entropy of activation"). As will be seen shortly, the former differs by a small amount only from the experimental activation energy of the reaction.

Equations (157) and (158) are of fundamental importance in bringing out the essential point that it is the free energy of activation, and not necessarily the heat of activation, which determines the rate of a chemical reaction. It is only because in many gas reactions the entropy factor does not vary greatly that the heat, or energy, of activation appears to be the important factor. It is evident from Eq. (158), however, that a large value of $T \Delta S^\ddagger$ can compensate for a high ΔH^\ddagger ; this is particularly the case for the denaturation of proteins (see page 442). The energy of activation is often exceptionally high, *e.g.*, 100 kcal. or more; but the reaction takes place with considerable velocity even at ordinary temperatures because the change is accompanied by a large increase of entropy. On the other hand, condensation of a vapor is a relatively slow process in spite of the small, or zero, heat of activation because of the marked decrease of entropy. In the former case the free energy of activation is relatively low, in spite of the high heat of activation, whereas in the latter case it is high, although the heat of activation is small. In general, any external factor that decreases the free energy of activation will increase the rate of reaction, the applied potential gradient has this effect in the discharge of ions (page 576), and electric fields due to ions or other charged species have an analogous influence on many reactions in solution (Chap. VIII). If ΔF^\ddagger is the increase of free energy on activation due to internal factors and $\Delta F_{\text{ext.}}^\ddagger$ is that brought about by external factors, such as those just mentioned, the specific-rate equation becomes

$$k = \frac{kT}{h} e^{-\Delta F^\ddagger/RT} e^{-\Delta F_{\text{ext.}}^\ddagger/RT} \quad (159)$$

In accordance with the foregoing discussion a catalyst is a substance that permits a homogeneous reaction to take place by a path requiring a lower free energy of activation than normal (see also page 438).⁷

Experimental Activation Energy.—For practical purposes, it is desirable to write Eq. (158) in a form containing the experimental activation energy (page 194) in place of ΔH^\ddagger ; but before doing so it is necessary to decide on the unit employed for expressing the specific reaction rate, for this determines the standard state. If pressure units, *e.g.*, atmospheres, are employed, Eq. (142) may be written in the logarithmic form

$$\ln k_p = \ln \frac{k}{h} + \ln T + \ln K_p^\ddagger, \quad (160)$$

and differentiation with respect to temperature gives

$$\frac{E_p}{RT^2} \quad \frac{d \ln k_p}{dT} = \frac{1}{T} + \frac{d \ln K_p^\ddagger}{dT} \quad (161)$$

$$= \frac{1}{T} + \frac{\Delta H^\ddagger}{RT^2}. \quad (162)$$

$$\therefore E_p = RT + \Delta H^\ddagger, \quad (163)$$

where E_p is the corresponding experimental activation energy. In these equations, ΔH^\ddagger is not the value for the standard state; however, for a system that behaves ideally ΔH^\ddagger is independent of the standard state, and so the difference may be disregarded. For the chosen standard state, Eq. (158) becomes

$$k_p = \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S_p^\ddagger/R}, \quad (164)$$

the suffix p being unnecessary for ΔH^\ddagger , as just explained. Introducing the value of ΔH^\ddagger as given by Eq. (163) into (164) yields

$$k_p = e \frac{kT}{h} e^{-E_p/RT} e^{\Delta S_p^\ddagger/R}. \quad (165)$$

If the specific reaction rate k is expressed in terms of concentrations, as is generally the case, the corresponding equation

⁷ Cf. A. E. Stearn, H. P. Johnston and C. R. Clark, *J. Chem. Phys.*, **7**, 970 (1939).

for the experimental activation energy* E , is

$$\frac{E_{\text{exp.}}}{RT^2} \cdot \frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln K_c^\ddagger}{dT} \quad (166)$$

$$\therefore E_{\text{exp.}} = RT + \Delta E^\ddagger \quad (167)$$

$$= RT + \Delta H^\ddagger - p \Delta v^\ddagger, \quad (168)$$

where ΔE^\ddagger is the increase of internal energy for the activation process, and this is equal, thermodynamically, to $\Delta H^\ddagger - p \Delta v^\ddagger$, where Δv^\ddagger represents the accompanying increase of volume. Since the standard state is now unit concentration, the appropriate form of Eq. (158) is

$$k = \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S_c^\ddagger/R} \quad (169)$$

the standard state restriction for ΔH^\ddagger being omitted on the basis of the approximation that the system behaves ideally; insertion of the value of ΔH^\ddagger obtained from Eq. (168) gives

$$k = \frac{kT}{h} e^{-(E_{\text{exp.}} - RT + p \Delta v^\ddagger)/RT} e^{\Delta S_c^\ddagger/R} \quad (170)$$

For a gas reaction, $p \Delta v^\ddagger$ may be put equal to $\Delta n^\ddagger RT$, where Δn^\ddagger is the increase in the number of molecules when the activated state is formed from the reactants; and so Eq. (170) may be written

$$k = e^{-(\Delta n^\ddagger - 1)} \frac{kT}{h} e^{-E_{\text{exp.}}/RT} e^{\Delta S_c^\ddagger/R} \quad (171)$$

Since the quantity ΔS_c^\ddagger , with unit concentration as the standard state, is a somewhat unusual way of expressing entropy changes for gaseous systems, it is useful to employ ΔS_p^\ddagger instead. It can be shown thermodynamically that for an ideal gas system

$$\Delta S_c = \Delta S_p - \Delta n R \ln RT, \quad (172)$$

and hence in this particular instance

$$e^{\Delta S_c^\ddagger/R} = e^{\Delta S_p^\ddagger/R} (RT)^{-\Delta n^\ddagger}, \quad (173)$$

so that Eq. (171) becomes

$$k = e^{-(\Delta n^\ddagger - 1)} \frac{kT}{h} e^{-E_{\text{exp.}}/RT} e^{\Delta S_p^\ddagger/R} (RT)^{-\Delta n^\ddagger} \quad (174)$$

* Since concentration units are commonly employed, the suffix c will not be appended.

If the rate equation involves x molecules of reactant, *i.e.*, the process is one of the x th order, and the activated complex involves all of them, Δn^\ddagger is equal to $-x + 1$; and hence Eq. (173) may be written

$$k = e^x \frac{kT}{h} e^{-E_{\text{exp.}}/RT} e^{\Delta S_p^\ddagger/R} (RT)^{x-1}. \quad (175)$$

The same result may be obtained directly from Eq. (165) by making use of the fact that k (for concentration units) is equal to $k_p(RT)^{x-1}$; and hence $E_{\text{exp.}}$ (for concentration units) is equal to $E_p + (x - 1)RT$.

For a bimolecular gas reaction, x is 2 and Δn^\ddagger is -1 ; and so Eqs. (171) and (175) become

$$k = e^2 \frac{kT}{h} e^{-E_{\text{exp.}}/RT} e^{\Delta S_p^\ddagger/R},$$

and

$$k = e^2 \frac{kT}{h} e^{-E_{\text{exp.}}/RT} e^{\Delta S_p^\ddagger/R} RT, \quad (176)$$

respectively.

For a unimolecular gas reaction, x is 1 and Δn^\ddagger is zero; and hence,

$$k = e \frac{kT}{h} e^{-E_{\text{exp.}}/RT} e^{\Delta S^\ddagger/R}, \quad (177)$$

the value of ΔS^\ddagger being independent of the standard state. As is to be expected, the same expression is applicable to k and k_p , since the specific rate of a first-order reaction is independent of the units employed, and hence of the standard state.

For reactions *in solution*, it is invariably the practice to use concentration terms; therefore, the only standard state that need be considered is that of unit concentration (or unit activity). It is necessary to employ Eq. (170); and since $\Delta \nu^\ddagger$ is virtually zero in solution, it follows that

$$= e \frac{kT}{h} e^{-E_{\text{exp.}}/RT} e^{\Delta S_e^\ddagger/R}, \quad (178)$$

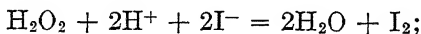
for all reactions occurring in ideal liquid systems.

CONSECUTIVE REACTIONS

The Activated State.—For a series of consecutive reactions (*cf.* page 99) the over-all rate is determined by the rate of passage

of activated complexes over the highest energy barrier, *viz.*, *C* in Fig. 19, page 100. From the standpoint of the theory of absolute reaction rates, it is sufficient, provided that equilibrium is established between the various intermediates, to consider only the equilibrium between the initial state and the rate-determining activated state, *i.e.*, the one at the top of the highest barrier; all intermediate stages and activated states can be neglected. Equations (141) and (142) are thus applicable to a set of consecutive reactions, provided that F_{\ddagger} in (141) applies to the rate-determining activated complex, generally referred to as "the activated state for the reaction," and E_0 is the difference in energy, between the zero-value levels, of this activated state and the initial reactants. The quantity E_0 is the equivalent of E in Fig. 19, after making allowance for the zero-point energies. In Eq. (142), similarly, K^{\ddagger} refers to the equilibrium between the activated state for the reaction and the initial state.*

One of the consequences of these conclusions is that the formula of the rate-determining activated complex for a series of reactions can be derived from the kinetics of the over-all reaction. If the rate of reaction between A and B is determined by c_A^x and c_B^y , then the activated complex must have the formula A_xB_y ; this result follows directly from Eq. (142). It is often found, especially in complicated reactions, which undoubtedly take place in stages, that the observed order of the reaction is much less than the stoichiometric equation would suggest. This means that the rate-determining stage involves a few molecules only and the corresponding activated complex is relatively simple. An example of this type of reaction is that between hydrogen peroxide and hydriodic acid, *viz.*,



the kinetics of the reaction show the rate to be directly proportional to the concentrations of the peroxide and iodide ions. It is evident, therefore, that the activated complex has the formula

* For purposes of calculation, any of the maxima in Fig. 19 could have been chosen as the activated state; if the one chosen is below the highest one, however, it would be necessary to introduce an additional transmission coefficient which would be equal to $e^{-\Delta F/RT}$, where ΔF is the free-energy difference between the highest maximum and the one chosen.

$\text{H}_2\text{O}_2\text{I}^-$. When one of the reactants has no influence on the kinetics of the process, *e.g.*, iodine in the iodination of acetone, that substance does not form part of the rate-determining activated complex; it is concerned, therefore, only in one or more of the rapid stages that do not affect the measured reaction rate.

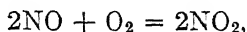
CHAPTER V

HOMOGENEOUS GAS REACTIONS

Introduction.—According to the arguments developed in the previous chapters the specific rate constant of any chemical reaction may be expressed in terms of certain universal constants, the moments of inertia and normal vibration frequencies of the initial and activated states and the energy of activation of the process. All these quantities can, in theory, be derived directly from spectroscopic data and from the potential-energy surface of the reacting system, which is also based on spectroscopic data. It is therefore possible in principle, to calculate the specific reaction rate of a chemical reaction, provided that the necessary spectroscopic information is available. The calculation of reaction rates in this manner is the objective toward which the treatment of the earlier chapters of this volume has been directed, but it is in relatively few instances only that this result can be achieved without reference to any experimental data based on actual measurements of reaction rates.

The specific rate of a reaction may be expressed in the form of the general equation $k = A e^{-E/RT}$; and, as seen in Chap. I, the problem of reaction rates falls into two parts; one the calculation of E and the other the evaluation of the A term. It is true that, according to the statistical treatment of Chap. IV, the latter involves the moments of inertia and vibration frequencies of the activated complex which, like the activation energy E , are obtained from the potential-energy surface; this connection between A and E is, however, only incidental, for it might be possible, theoretically, to derive the quantities necessary to calculate A in an entirely independent manner. It follows, therefore, that there are two separate aspects to the problem of reaction rates; and even when it is not possible to combine them so as to calculate the specific rate constant absolutely, it is still interesting to compute one factor or the

other. For example, in some instances, as in the case of the reaction



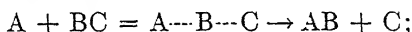
the statistical part of the calculations, which gives the A factor in the rate equation, may be carried through, but the activation energy has to be taken from experimental measurements of the temperature coefficient of the reaction velocity. In other cases, however, the activation energy can be derived from the potential-energy surface, but the transmission coefficient κ may be in doubt. Some indication of its value may then be obtained by comparing the calculated rate, on the assumption that κ is unity, with the experimental reaction rate.

HYDROGEN ATOM-MOLECULE REACTIONS¹

Reaction-rate Equations.—The most complete application of the method for calculating reaction rates has been made in connection with processes of the ortho-para-hydrogen conversion type, involving an atom and a molecule of hydrogen or deuterium. Ten such reactions are possible, *viz.*:

- (1) $\text{H} + o\text{-H}_2 = p\text{-H}_2 + \text{H}$, and the reverse,
- (2) $\text{D} + p\text{-D}_2 = o\text{-D}_2 + \text{D}$, and the reverse,
- (3) $\text{H} + \text{DH} = \text{HD} + \text{H}$,
- (4) $\text{D} + \text{HD} = \text{DH} + \text{D}$,
- (5) $\text{H} + \text{HD} = \text{H}_2 + \text{D}$,
- (6) $\text{D} + \text{H}_2 = \text{HD} + \text{H}$,
- (7) $\text{D} + \text{DH} = \text{D}_2 + \text{H}$,
- (8) $\text{H} + \text{D}_2 = \text{HD} + \text{D}$.

These may be represented by the general equation



and the velocity constant is given by the appropriate form of Eq. (149), page 193, thus,

$$k = \kappa i_n \frac{g_{\text{ABC}}}{g_{\text{A}}g_{\text{BC}}} \left[\frac{M}{m_{\text{A}}(m_{\text{B}} + m_{\text{C}})} \right]^3 \frac{I_{\text{ABC}}}{I_{\text{BC}}} \cdot \frac{\sigma_{\text{BC}}}{\sigma_{\text{ABC}}} \cdot \frac{h^2}{(2\pi)^{3/2} (kT)^{1/2}} \frac{1}{1 - e^{-h\nu_{\text{BC}}/kT}} e^{-E_0/RT} \quad (1)$$

$$\prod (1 - e^{-h\nu_{\text{ABC}}/kT})$$

¹ H. Eyring and M. Polanyi, *Z. physik. Chem.*, **B**, **12**, 279 (1931); J. O. Hirschfelder, H. Eyring and B. Topley, *J. Chem. Phys.*, **4**, 170 (1936); see also L. Farkas and E. Wigner, *Trans. Faraday Soc.*, **32**, 708 (1936).

where M is equal to the sum of atomic masses, $m_A + m_B + m_C$; the factor for the penetration of the barrier (page 191) is omitted. In Eq. (1), m_A , m_B and m_C are the masses of the atoms A, B and C, respectively, and the suffixes BC and ABC, as applied to the number of electronic states g , to the moments of inertia I , to the symmetry numbers σ and to the vibration frequencies ν , refer to the molecule BC and the activated complex A—B—C, respectively. It will be observed that Eq. (1) includes a factor i_n which does not appear in Eq. (149), Chap. IV. If there were no change in the ortho-para ratio in a reaction, this quantity would be unity; but as some of the reactions under consideration involve such a change, it is necessary to make the appropriate allowance. Since the equilibrium ratio of the concentrations of *o*-H₂ to *p*-H₂ is 3 to 1, it follows that the rate of the reaction $H + H_2(p) = H_2(o) + H$, must be three times as fast as the opposite reaction $H + H_2(o) = H_2(p) + H$. The sum of the rates of these two processes would give the value of the reaction rate if there were no change in the ortho-para ratio, *i.e.*, as given by Eq. (1) with i_n equal to unity. It follows, therefore, that in the para- to ortho-H₂ conversion i_n is $\frac{3}{4}$ and in the ortho- to para-H₂ conversion it is $\frac{1}{4}$. The equilibrium ratio of ortho- to para-deuterium is 2. Therefore, in the conversion of the para- to ortho-form, i_n is $\frac{2}{3}$; in the reverse reaction, $\frac{1}{3}$. In general, i_n is equal to the ratio of the statistical weight, due to nuclear spin (see page 172) of the resultant, to the total for reactant and resultant. For the six reactants above that are not accompanied by an ortho-para change, the factor i_n is unity.

The normal frequency ν_{BC} is the vibration frequency of the diatomic molecule BC; and the three frequencies of the activated complex, referred to as ν_{ABC} , are ν_s , which is the stretching frequency whose square is real, and the doubly degenerate bending frequency ν_ϕ (page 120). The vibrational-partition-function portion of Eq. (1) may therefore be written

$$\frac{1 - e^{-h\nu_{BC}/kT}}{3 \prod (1 - e^{-h\nu_{ABC}/kT})} \quad \frac{1 - e^{-h\nu_{BC}/kT}}{(1 - e^{-h\nu_s/kT})(1 - e^{-h\nu_\phi/kT})^2} \quad (2)$$

If the activation energy E_0 in Eq. (1) is replaced by E_c , the classical activation energy, then, by the method described on page 194, it follows that (1) may now be written in the form

$$k = \kappa i_n g_A g_{BC} \left[m_A (m_B + m_C) \right]^{3/2} \frac{I_{ABC}}{I_{BC}} \cdot \frac{\sigma_{BC}}{\sigma_{ABC}} \cdot \frac{h^2}{(2\pi)^{3/2} (kT)^{1/2}} \cdot \frac{1}{4} \frac{\sinh \frac{1}{2}(\hbar \nu_{BC}/kT) e^{-E_c/RT}}{\sinh \frac{1}{2}(\hbar \nu_s/kT) [\sinh \frac{1}{2}(\hbar \nu_\phi/kT)]^2} \quad (3)$$

The moments of inertia of the activated complex, I_{ABC} , and of the molecule BC, I_{BC} , are

$$I_{ABC} = \frac{1}{M} [m_A(m_B + m_C)r_{AB}^2 + 2m_A m_B r_{AB} r_{BC} + m_C(m_A + m_B)r_{BC}^2], \quad (4)$$

where r_{AB} and r_{BC} are the distances apart of A and B and of B and C in the activated complex; and

$$I_{BC} = \frac{m_B m_C}{m_B + m_C} (r_0)_{BC}^2, \quad (5)$$

where $(r_0)_{BC}$ is the equilibrium separation of the atoms B and C in the molecule BC. The masses employed in Eqs. (3), (4) and (5) are the actual masses of the atoms, and the resulting specific rate constant is in cc. molecule⁻¹ sec.⁻¹ units. To convert into the more usual cc. mole⁻¹ sec.⁻¹ units, it is necessary to multiply by the Avogadro number.

Energy of Activation, Etc.—The values of m_A , m_B and m_C , which for the present series of reactions are either m_H or m_D , are known and are 1.67×10^{-24} g. and 3.34×10^{-24} g., respectively; and $(r_0)_{BC}$, the equilibrium internuclear distance, *i.e.*, 0.74 Å., is the same for H₂, HD and D₂. The normal vibration frequencies of the diatomic molecules are known from spectroscopic measurements to be 4,415.6 cm.⁻¹ for H₂, 3,825.0 for HD and 3,124.1 for D₂. From the potential-energy surface based on the assumption of a linear activated complex and 20 per cent coulombic energy, the dimensions of the activated state are found to be $r_{AB} = 1.354$ Å., and $r_{BC} = 0.753$ Å.* Hence, the moment of inertia I_{ABC} can be readily calculated for any of the isotopic reactions by means of Eq. (4). The vibration frequencies of

* Provided the configuration of the activated complex remains unchanged, as in the cases under consideration, the potential-energy surface is the same for all isotopic forms of the atoms involved: the equilibrium potential energy and dimensions of the activated complex are thus also independent of the isotope concerned.

the activated complexes can be derived from the potential-energy surface; the force constants f_{11} , f_{22} , f_{12} and f_ϕ (page 120) are the same for all the isotopic molecules, and once these are found it is only a matter of inserting the correct masses in the equations for the theory of small vibrations (page 115) in order to obtain the required frequencies.

The value of E_c as derived from the potential-energy surface referred to above is 7.63 kcal., and this is independent of the nature of the isotope involved because the potential-energy surface is almost the same in each case. The activation energy E_0 can now be obtained by the relationship (page 98)

$$E_0 = E_c + N(\sum \frac{1}{2} h \nu_{\ddagger} - \sum \frac{1}{2} h \nu_i),$$

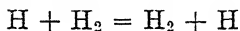
where ν_{\ddagger} refers to the vibration frequencies of the activated state, excluding the one having an imaginary value, and ν_i refers to the initial state. The results obtained in this way are given in Table VI. It should be noted that in computing the zero-point energy $\frac{1}{2} \sum h \nu_{\ddagger}$ of the activated state, the contribution of the doubly degenerate bending frequency ν_ϕ must be included twice. The moments of inertia of the activated complexes are also included in the table. According to these results the energy of activation of the ortho-para hydrogen conversion should be 8.5 kcal. This is in excellent agreement with the conclusion

TABLE VI.—ACTIVATION ENERGIES OF HYDROGEN MOLECULE-ATOM REACTIONS

Reaction	I_{ABC} g. cm. ² $\times 10^{40}$	$\frac{1}{2} N h \nu_\phi$, kcal.	$\frac{1}{2} N h \nu_s$, kcal.	Zero-point energy, kcal.		E_0 , kcal.
				Acti- vated state	Initial state	
(1) H + H ₂	3.79	0.95	5.18	7.08	6.21	8.50
(2) D + D ₂	7.58	0.67	3.66	5.00	4.39	8.24
(3) H + DH	4.69	0.86	4.57	6.29	5.38	8.54
(4) D + HD	7.50	0.86	4.38	6.10	5.38	8.35
(5) H + HD	4.92	0.88	4.40	6.16	5.38	8.41
(6) D + H ₂	5.45	0.93	5.17	7.03	6.21	8.45
(7) D + DH	5.77	0.76	4.56	6.08	5.38	8.33
(8) H + D ₂	4.92	0.70	3.67	5.07	4.39	8.31

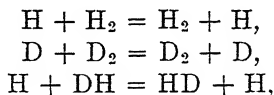
drawn from both high and low temperature measurements of the reaction rates.²

There now remains only a consideration of the factors κ , g and σ before all the data are available for the calculation of the specific reaction rate by means of Eq. (3). The electronic statistical weight g_A for atomic hydrogen is 2 (page 172), and g_{BC} for molecular hydrogen is 1. It is reasonable to assume, therefore, that g_{ABC} for the activated complex is 2, so that the electronic factor $g_{ABC}/g_A g_{BC}$ is equal to unity. The symmetry number σ_{BC} of the initial molecule BC is 2 if BC is either H_2 or D_2 , but it is unity when BC is HD. It will be seen from Fig. 27 that the potential-energy surface for the reaction

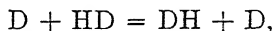


makes the activated complex unsymmetrical; the symmetry number σ_{ABC} must therefore be unity in all the cases under consideration.

Transmission Coefficients.—If the potential-energy surface calculated by the semi-empirical method for the hydrogen atom-molecule reaction is correct, then for the symmetrical reactions, *viz.*,



and



the transmission coefficient κ should be $\frac{1}{2}$. This conclusion is drawn from the fact that the basin at the top of the potential-energy pass, which represents the metastable molecule ABC, is quite symmetrical; the two gaps in the basin, leading to the two valleys representing initial and final states, respectively, are thus at the same level. A mass point wandering round the basin, as indicated in Fig. 28, will have an equal probability of passing out through each gap; it is evident, therefore, that only one-half of the activated complexes, arriving from the valley representing the initial reactants, will pass into the valley representing the resultants. The transmission coefficient will, therefore, be one-

² K. H. Geib and P. Harteck, *Z. physik. Chem. (Bodenstein Festband)*, 849 (1931); A. Farkas and L. Farkas, *Proc. Roy. Soc.*, **152**, A, 124 (1935).

half, as indicated above. For the unsymmetrical reactions, the two gaps in the potential-energy basin at the top of the pass will not be at the same level; the probability that the system will enter one valley will, therefore, not be the same as for the other, and the transmission coefficient will differ from one-half. To evaluate this factor, it is assumed that when the system is in the energy basin its chances of decomposing in the two different ways, *i.e.*, of passing out through the two gaps, is independent of the direction in which the system entered the basin. This assumption is equivalent to postulating that $\kappa_f + \kappa_r = 1$, where κ_f and κ_r refer to the forward and reverse reactions, respectively.* If G_f and G_r are the specific reaction rates for the two reactions, except for the transmission coefficients, then

$$k_f = \kappa_f G_f \quad \text{and} \quad k_r = \kappa_r G_r, \quad (6)$$

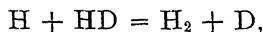
where k_f and k_r are the actual specific rates. Since the equilibrium constant K of any reaction is equal to the ratio of the rates of the forward and reverse directions, it follows that

$$K = \frac{k_f}{k_r} = \frac{\kappa_f G_f}{\kappa_r G_r}; \quad (7)$$

and since $\kappa_f + \kappa_r = 1$,

$$\kappa_f = \frac{G_r K}{G_f + G_r K} \quad \text{and} \quad \frac{G_f K}{G_f + G_r K}. \quad (8)$$

To evaluate the transmission coefficients, it is necessary to know the equilibrium constant for the particular reaction; this is readily derived by the use of Eq. (3). For the reaction (5),



for example, the equilibrium constant can be obtained by means of the partition functions of the initial and final states (page 181); thus,

$$K = \frac{F_{\text{H}_2} \times F_{\text{D}}}{F_{\text{H}} \times F_{\text{HD}}} e^{-\Delta \epsilon_0 / RT}, \quad (9)$$

* If there were no basin at the top of the energy pass, and hence only one activated complex at the saddle, for both forward and reverse directions, κ_r and κ_f would have to be equal; they would then probably both be close to unity.

where the F terms do not include the zero-point energies. By introducing the usual values for the partition functions and incorporating the zero-point energies in the vibrational factor (*cf.* page 183), it is found that

$$K_{\text{H+HD}} = \frac{\sigma_{\text{HD}}}{\sigma_{\text{H}_2}} \cdot \frac{2m_{\text{D}}}{m_{\text{H}} + m_{\text{D}}} \cdot \frac{\sinh \frac{1}{2}(\hbar\nu_{\text{HD}}/kT)}{\sinh \frac{1}{2}(\hbar\nu_{\text{H}_2}/kT)}, \quad (10)$$

from which K may be readily determined at any required temperature. By means of Eqs. (3) and (8), it is now possible to calculate κ for reactions (5) and (6), *i.e.*, κ_5 and κ_6 . The values of κ_7 and κ_8 , the latter being equal to $1 - \kappa_7$, may be obtained in an analogous manner; some of the results for κ_5 and κ_7 are given in Table VII.

TABLE VII.—TRANSMISSION COEFFICIENTS FOR HYDROGEN MOLECULE-ATOM REACTIONS

Temperature	300°K.	600°K.	900°K.	1000°K.
κ_5	0.192	0.332	0.383	0.396
κ_7	0.819	0.673	0.621	0.621

Utilizing the various data derived above, the rates of the eight exchange reactions are given in Table VIII for a series of temperatures; for the purpose of comparison with the other reactions, the figures for reactions (1) and (2) give the sum, in each case, of the conversion of ortho- to para-forms and the reverse.

Discussion.—Where the experimental data are available, the agreement between observed and calculated reaction rates is very satisfactory; it is, nevertheless, important to consider how far this agreement is fortuitous. The calculated activation energy derived from the potential-energy surface is very close to the actual value, as already mentioned; but it must be remembered that the calculated figure is based on an assumed proportion, *viz.*, 20 per cent, of the total binding energy as being coulombic in nature. It is true that a different proportion would alter the activation energy to some extent; but the essential point is that the proportion of 20 per cent is not unreasonable, and hence it is seen that *by making a reasonable assumption* it is

TABLE VIII.—REACTION RATES
(cc. mole⁻¹ sec.⁻¹ units)

Reaction		300°K. $k \times 10^{-7}$	600°K. $k \times 10^{-10}$	1000°K. $k \times 10^{-12}$
(1) $H + H_2 = H_2 + H$.	Calc.....	7.3	7.3	1.5
	Obs ^{3,4}	9.0	...	2.2
(2) $D + D_2 = D_2 + D$.	Calc.....	3.0	3.5	0.76
	Obs ⁴	1.2
(3) $H + DH = HD + H$.	Calc.....	2.2	2.6	0.52
	Obs ⁴	0.68
(4) $D + HD = DH + D$.	Calc.....	2.4	2.4	0.44
	Obs ⁴	1.0
(5) $H + HD = H_2 + D$.	Calc.....	1.1	1.8	0.45
	Obs ⁴	0.95
(6) $D + H_2 = DH + H$.	Calc.....	7.1	6.2	1.2
	Obs ⁴	2.5
(7) $D + DH = D_2 + H$.	Calc.....	3.0	2.5	0.50
	Obs ⁴	0.79
(8) $H + D_2 = HD + D$.	Calc.....	1.5	2.6	0.74
	Obs ⁴	1.2

possible to calculate an activation energy which is a good approximation to the experimental value.

Mention has been made of the fact that in the unsymmetrical reactions the two saddle points, *i.e.*, the gaps in the basin at the top of the energy barrier, do not correspond to the same energy; in the calculations described above the value used for the activation energy was based on the height of the first saddle point encountered. It has been suggested⁵ that the greater of the two energies should be employed, because the system must, in any case, pass over both points before it can react, and the transmission coefficient should then be taken as unity. The

³ Geib and Harteck, Ref. 2.

⁴ Farkas and Farkas, Ref. 2.

⁵ E. A. Guggenheim and J. Weiss, *Trans. Faraday Soc.*, **34**, 57 (1938).

difference arising in this connection is very small, not more than 0.25 kcal. (see Table VI) and is compensated for by the allowance made for the deviation of the transmission coefficient from unity.

The activation energies for the series of atom-molecule reactions involving hydrogen and deuterium are obviously not very different, and so the actual variations in the specific rate constant are determined mainly by the statistical, or frequency, factor. It has been pointed out that almost as good agreement between theory and experiment for the relative rates of the eight reactions in Table VIII could be obtained on the basis of the collision theory of reaction velocity, *i.e.*, by taking the collision factor as proportional to $[M/m_A(m_B + m_C)]$, where M , m_A , m_B and m_C have the same significance as in Eq. (2), and introducing a factor 2 for reactions involving H_2 or D_2 , since collisions at either end would lead to the same result.⁶ This treatment is equivalent to ignoring the terms in Eq. (3) involving the vibration frequencies and assuming that the ratio of the moments of inertia, I_{ABC}/I_{BC} , is equal to $m_A(m_B + m_C)/M$. It happens, in the particular reactions under discussion, because of the nature of the substances concerned, that this approximation can be made without serious error; but this does not invalidate the method based on the theory of absolute reaction rates as given in Chap. IV. If it can be shown that *in every case* the collision theory gives results which are as good as, or better than, those derived from statistical considerations, then the latter method of calculation might be regarded as unnecessary, but nevertheless not incorrect. It will be shown, however, that the reaction-rate theory described here succeeds where the collision theory fails completely to give an adequate interpretation of measurements of reaction velocities. The criticism considered above cannot therefore be regarded as invalidating the theory of absolute reaction rates.

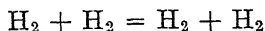
HYDROGEN-MOLECULE REACTIONS⁷

Exchange Reactions.—When para-hydrogen or ortho-deuterium is heated at a temperature of about 600°C., the equilibrium between ortho- and para-forms is established relatively

⁶ Guggenheim and Weiss, Ref. 5.

⁷ H. Eyring, *J. Am. Chem. Soc.*, **53**, 2537 (1931); J. O. Hirschfelder and F. Daniels (private communication).

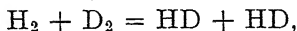
rapidly; the over-all reactions are



and



respectively. Similarly, if a mixture of molecular hydrogen and deuterium is heated, the equilibrium concentration of hydrogen deuteride (HD) is soon formed, so that the reaction, analogous to those just mentioned, *viz.*,



occurs readily. The fact that the apparent order of the reaction is found to be close to 1.5 in each case shows that the processes

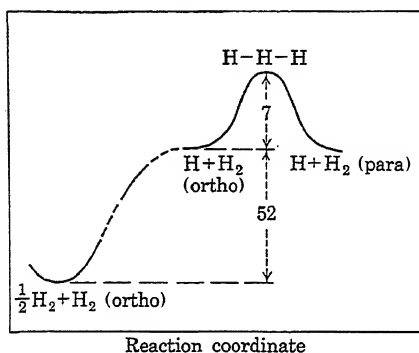
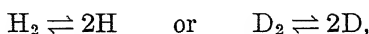
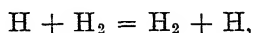


FIG. 54.—Effective activation energy for the ortho-para conversion of molecular hydrogen or deuterium.

do not involve two molecules of hydrogen (or deuterium), for if so the reactions would be of the second order. It appears, therefore, that there is a rapid establishment of an equilibrium between hydrogen (or deuterium) molecules and atoms, thus,



followed by reactions of the type

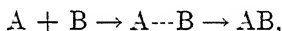


which have been considered above. The activation energy of this stage is known to be about 7 kcal., but since the formation of the equilibrium concentration of 1 g.-atom of hydrogen atoms from molecules requires the supply, to the latter, of half the heat of dissociation per mole of hydrogen, *i.e.*, about 52 kcal., it

follows that the effective energy of activation for the three reactions considered above is $52 + 7$ kcal., *i.e.*, approximately 59 kcal. (*cf.* Fig. 54). If this argument is correct, the activation energy for the reaction between two molecules of hydrogen (or deuterium) should be appreciably greater than this value. Calculations have been made for this reaction by the semi-empirical method, treating the system as one of four electrons; the activation energy is found to be approximately 90 kcal., based on the assumption of 10 per cent coulombic energy, and hence is in agreement with expectation.

COMBINATION OF HYDROGEN ATOMS³

Reaction in Absence of Third Body.—For the reaction between two atoms A and B, *viz.*,



the theory of absolute reaction rates gives

$$k_2 = \kappa i_n \frac{g_{AB}^\ddagger}{g_A g_B} \cdot \frac{\left[\frac{2\pi(m_A + m_B)kT}{h^3} \right]^{3/2}}{\left[\frac{(2\pi m_A kT)^{3/2}}{h^3} \right] \left[\frac{(2\pi m_B kT)^{3/2}}{h^3} \right]} \cdot \frac{\sum_{J=0}^{\infty} (2J+1) e^{-\epsilon_J^*/kT}}{\sigma_{AB}^\ddagger} \cdot \frac{kT}{h} \quad (11)$$

where the g and i_n terms are, as previously, the electronic and nuclear spin statistical weights and σ_{AB}^\ddagger is the symmetry number of the activated complex; since A and B are atoms, their symmetry numbers are unity. Apart from the translational energy, the partition function for the activated complex contains terms for rotational energy only, since the single degree of vibrational freedom generally possessed by a diatomic molecule is here replaced by translation in the coordinate of decomposition. If the initial state of the system, *i.e.*, the separated atoms, is taken as the zero of energy, then the rotational contribution to the partition function is $\sum (2J+1) e^{-\epsilon_J^*/kT}$, where ϵ_J^* is $\epsilon_J - (D - \epsilon_v)$,

³ H. Eyring, H. Gershinowitz and C. E. Sun, *J. Chem. Phys.*, **3**, 786 (1935).

as seen from Fig. 37 (page 130). As explained in Chap. III, the actual rotational energy ϵ_J is given by $\epsilon_J = J(J+1)\hbar^2/8\pi^2 I_{\ddagger}$, where I_{\ddagger} , the moment of inertia in the activated state, is equal to μr_J^2 , the interatomic distance r_J in the complex being obtained by the method already described (page 127). The value of D , the dissociation energy, should be known, and ϵ_v is obtained from the potential-energy curve, or from the Morse equation, for the stable molecule AB. It should be noted that since the separated atoms by assumption have zero energy the corresponding term $e^{-E_0/RT}$ does not appear in Eq. (11).

For the reaction $\text{H} + \text{H} = \text{H}_2$, the nuclear spin factor i is unity, since the ortho-para equilibrium will always be established in the system. The electronic statistical weight g_{AB} of the activated state, which is virtually H_2 , may be taken as the same as for molecular hydrogen, *i.e.*, unity, whereas the values of g_A and g_B for atomic hydrogen are each 2. Since the activated state is a symmetrical molecule, the symmetry number σ_{AB}^\ddagger will be 2.

Upon inserting the data in Eq. (11) and multiplying by N to obtain the specific reaction rate k_2 in cc. mole⁻¹ sec.⁻¹, it is found that

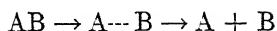
$$k_2 = \kappa \times 2.78 \times 10^{14}. \quad (12)$$

Unfortunately, there is no direct method of evaluating the transmission coefficient κ , and consequently it is necessary to speculate concerning its magnitude. When the two hydrogen atoms combine to form a molecule, the heat evolved in the reaction, which is more than 100 kcal. per mole, must be dissipated if the molecule is to be stable. As long as this energy is in the vibrational degree of freedom, there is complete certainty that in the course of a vibration the molecule will redissociate into atoms. The value of κ depends, therefore, on the ratio of the time of oscillation and the time elapsing before the molecule can lose part of its excess energy. It appears that for a diatomic oscillator with a dipole of reasonable size the time elapsing before it loses its excess energy is about 10^{-2} to 10^{-3} sec. For a substance like hydrogen, which has no dipole moment but only a quadrupole moment, the mean life of the vibrationally excited molecule may well be of the order of 1 sec. Since the vibration frequency is about 10^{14} sec.⁻¹, it is evident that an excited hydrogen

molecule would radiate its excess energy, on the average, once in 10^{14} oscillations. The probability that a molecule formed from two hydrogen atoms will not dissociate is thus 10^{-14} , and hence the transmission coefficient κ will be of this order of magnitude. If κ in Eq. (12) is taken as 10^{-14} , the specific rate for the combination of hydrogen atoms would be 3 cc. mole⁻¹ sec.⁻¹; although this quantity has not been determined experimentally, it is known that on a glass surface⁹ the specific rate is about 10^5 cc. mole⁻¹ sec.⁻¹. A difference of this order between the homogeneous and heterogeneous reactions is not unreasonable.

It is on account of the relatively long life of an excited oscillator that reactions between two atoms, without the intervention of a third body, are much less common than was at one time expected. If the excited molecule is deprived of its excess energy in a collision with another atom or molecule, then it may be stabilized. It is for this reason that the recombination of atoms almost invariably occurs by way of a three-body collision; some aspects of this subject have been discussed in Chap. III, and further reference to the reaction between three hydrogen atoms will be made below. The combination of two free radicals might, at first sight, be thought to be similar to the reaction between two atoms; the difference, however, lies in the fact that in the former case, provided that the free radical is relatively complex,* the resulting molecule has many vibrational degrees of freedom, and a redistribution of energy between them occurs in a relatively short space of time. The energy can then be removed in a collision before it can return to the bond at which the redissociation process would otherwise occur.

Dissociation of Molecular Hydrogen.¹⁰—The dissociation reaction



involves the same activated state as the reverse process just considered. The partition function, the energy of the separated atoms being taken as the zero level, is the same as the numerator in Eq. (11), and hence the specific reaction rate k_1 is given by

⁹ I. Amdur, *J. Am. Chem. Soc.*, **62**, 2347 (1938).

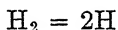
* The combination of methyl radicals in pairs requires the presence of a third body.

¹⁰ Eyring, Gershinowitz and Sun, Ref. 8.

$$k_1 = \kappa i_n \frac{g_{AB}^\ddagger}{g_{AB}} \cdot \frac{[2\pi(m_A + m_B)kT]^{3/2}}{h^3} \cdot \frac{\sigma_{AB}}{\sigma_{AB}^\ddagger} \cdot \frac{\sum_{J=0}^{\infty} (2J+1) e^{-\epsilon_J^*/kT}}{\frac{8\pi^2 I_{AB} kT}{h^2}} \cdot \frac{1}{(1 - e^{-h\nu_{AB}/kT})^{-1}} \cdot \frac{1}{e^{D/RT}} \cdot \frac{kT}{h} \quad (13)$$

Attention may be called to the term $e^{D/RT}$ in the denominator; this arises because the energy of the initial state, a molecule of hydrogen, is $-D$ per mole with reference to the postulated energy zero; the term $e^{-E/RT}$ in the partition function thus becomes $e^{D/RT}$ in this instance. Just as for the atom combination reaction, i_n is unity, since there is no change in the ortho-para ratio. The terms g_{AB}^\ddagger/g_{AB} and $\sigma_{AB}/\sigma_{AB}^\ddagger$ are both also equal to unity, since the electronic multiplicities and the symmetry numbers are certainly the same in the initial and the activated molecules. Inserting the rotational partition function for the activated state, as found for the previous reaction, and knowing the moment of inertia and vibrational frequency of the molecule AB make it possible to evaluate the rate constant from Eq. (13).

In the reaction



it is found that

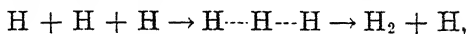
$$k_1 = \kappa \times 3.6 \times 10^{14} e^{-D/RT} \text{ sec.}^{-1}, \quad (14)$$

the rate constant being independent of the concentration units because the process is of the first order. Since the activated state is the same for both forward and reverse reactions and k_1/k_2 is equal to the equilibrium constant of the reaction $\text{H}_2 \rightleftharpoons 2\text{H}$, it can be readily seen that the transmission coefficient κ in Eqs. (11) and (13), and hence in Eqs. (12) and (14), must be the same. If this is taken, as before, to be about 10^{-14} , it follows that the specific rate for the dissociation of molecular hydrogen, k_1 , is approximately $3e^{-D/RT} \text{ sec.}^{-1}$. In view of the relatively large value of D , over 100,000 cal., this reaction will not have an appreciable velocity until very high temperatures are attained.

Three-atom Reactions.¹¹—It has been seen in the discussion on page 112 that there is a definite probability of three hydrogen

¹¹ Eyring, Gershinowitz and Sun, Ref. 8.

atoms reacting under certain conditions, thus,



to give an atom and a molecule. The rate of the reaction may be calculated by a method based on the theory of absolute reaction rates. In order that the activated complex, which is probably formed by the passage over a low rotational barrier as in the case of the combination of two hydrogen atoms, may pass into one valley, cross the median line and then find its way out of the other valley representing an atom and a molecule, it is necessary that the energy formed in the reaction should be properly distributed between two degrees of freedom (page 103). In writing the partition function of the activated state, therefore, the contribution of two of the vibrations is replaced by a factor H which gives the probability of the complexes having the required energy distribution for the reaction. According to the statistical theory of reaction rates the specific rate will be given by

$$k_3 = \kappa \frac{g_{\ddagger}}{g_i} \cdot \frac{[2\pi(m_1 + m_2 + m_3)kT]^{3/2}}{h^3} \cdot \frac{h^3}{(2\pi m_1 kT)^{3/2}} \cdot \frac{h^3}{(2\pi m_2 kT)^{3/2}} \cdot \frac{h^3}{(2\pi m_3 kT)^{3/2}} \cdot \prod_3 (1 - e^{-h\nu_{\ddagger}/kT})^{-1} \frac{8\pi^2 I_{\ddagger} kT}{h^2 \sigma_{\ddagger}} H \bar{v}. \quad (15)$$

where $\bar{v} = (kT/2\pi\mu)^{1/2}$ is the average velocity of the activated complexes across the median line of Fig. 27 (page 108). For the reaction of three identical, *e.g.*, hydrogen, atoms, the masses m_1 , m_2 and m_3 are of course equal. The symmetry numbers of the initial state have not been included in Eq. (15) since they are unity, and nuclear spin factors have been omitted since there is no ortho-para change. The electronic multiplicity g_{\ddagger} of the activated state is taken as 2, since the system of three atoms presumably has an unpaired spin, *i.e.*, $s = \frac{1}{2}$, and the multiplicity is $2s + 1$. Since each hydrogen atom has a multiplicity of 2, it follows that g_i is 8; hence, $g_{\ddagger}/g_i = \frac{1}{4}$. The symmetry factor σ_{\ddagger} is probably 2, since, on the assumption that the complex is linear, the activated state may be regarded as being situated on the median line of the potential-energy diagram, *i.e.*, when the distances r_1 and r_2 between pairs of adjacent atoms are

equal. It can be seen from Fig. 27 and the accompanying discussion that r_1 and r_2 must lie between about 1.5 and 4 Å.; for the purpose of calculating the moment of inertia I_{\ddagger} of the linear complex a mean value of 3 Å. may be employed. The value of μ , the reduced mass in the coordinate of decomposition, required for the evaluation of \bar{v} is not known with certainty; if the activated complex were moving parallel to the median line, the reduced mass in that direction would be $\frac{1}{2}m$, where m is the mass of each atom. On the other hand, if the motion were along a valley and parallel to either axis, μ would be $\frac{2}{3}m$, and hence the reduced mass is not likely to differ considerably from $0.6m$.

According to the methods of statistical mechanics,¹² the partition function factor H can be written as

$$H = h^{-2} \int_a^b dx \int_c^d dy \int_e^f dp_x \int_g^h dp_y e^{-} \quad (16)$$

where the integrals represent the weight factors and h^{-2} is for normalization purposes; x and y are the coordinates and p_x and p_y the corresponding momenta. The energy E is given by

$$E = \frac{1}{2}\mu(\dot{x}_1^2 + \dot{y}_1^2) + V(x_1, y_1), \quad (17)$$

μ being the reduced mass parallel to the axis, *i.e.*, $\frac{2}{3}m$; the first term on the right-hand side of Eq. (17) represents the kinetic energy and the second the potential energy of the mass point moving on the potential-energy surface. The limits of the integration are determined by the requirements of the distribution of energy before and after crossing the median line in order that reaction shall occur. By considering only systems having potential energy in excess of 45 kcal., *i.e.*, those requiring no activation energy, it is found that

$$H \approx \frac{2\mu kT}{h^2} \times 1.64 \times 10^{-8}.$$

If all systems crossing the median line actually reacted, the partition function, represented by H' , would be $2\pi\mu kTr_J/h^2$, where r_J is the distance between two hydrogen atoms at the rotation ridge representing the activated state (*cf.* page 127). The ratio H/H' may be taken as a measure of the transmission

¹² See, for example, R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," p. 79, Cambridge University Press, 1939.

coefficient, and using a value of 4.4×10^{-8} cm. for r_J , as indicated on page 131, κ is found to be $\frac{1}{8}$.

Before the rate constant can be evaluated by means of Eq. (15), it is only necessary to know the two vibration frequencies in the activated state; if they are very low, *e.g.*, 100 cm.^{-1} , then the classical value $kT/h\nu$ of the partition function may be used. Further, ν may be replaced by $(f/m)^{1/2}/2\pi$, where f is the force constant and m is related to the mass of the oscillator; hence, the partition function is $2\pi kTm^{1/2}/f^{1/2}h$. For the two degrees of vibrational freedom the partition function, included in the numerator of Eq. (15), will then be proportional to m . By taking into consideration the mass dependence of all the terms in Eq. (15), it is readily seen that, all other factors being equal, k_3 is proportional to $m^{-1/2}$. If the reaction of three hydrogen atoms is compared with that of three deuterium atoms, then provided that the vibrations are behaving classically, the ratio of the rates should be $\sqrt{2}$ to 1. This anticipation is in agreement with experiment,¹³ and so it may be assumed that the vibration frequencies in the activated state are about 100 cm.^{-1} . Upon introducing these and the other known values in Eq. (15), it is found that for three hydrogen atoms

$$k_3 \approx 3 \times 10^{15} \text{ cc.}^2 \text{ mole}^{-2} \text{ sec.}^{-1},$$

which may be compared with the experimental value of approximately $10^{16} \text{ cc.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$.¹⁴ The presence of a hydrogen atom, which is capable of carrying off some of the energy produced in the combination of two other hydrogen atoms, thus produces a very marked increase in the reaction rate.

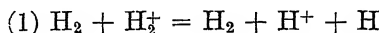
It was seen on page 115 that there is a possibility of the formation of a triangular activated complex as the result of two hydrogen atoms moving in a line and a third one coming toward them symmetrically in a direction at right angles. The rate of formation of molecular hydrogen by this mechanism will not be so great as that involving the linear complex considered above; since it provides an alternative mode of reaction, however, the rate must be added to that given above, but it will alter it by a factor of less than 2.

¹³ I. Amdur, *J. Am. Chem. Soc.*, **57**, 856 (1935).

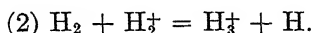
¹⁴ H. M. Smallwood, *ibid.*, **56**, 1542 (1934); Amdur, Ref. 13; *J. Am. Chem. Soc.*, **60**, 2347 (1938); W. Steiner, *Trans. Faraday Soc.*, **31**, 623 (1935).

HYDROGEN MOLECULE-ION REACTIONS¹⁵

The Formation of H_3^+ .—It is of interest in connection with reactions taking place in hydrogen exposed to α -particles to have information concerning the relative rates of the reactions



and



The former is undoubtedly slow since the process is endothermic to the extent of approximately 61 kcal., and so the activation energy must be at least this amount; at ordinary temperatures, therefore, reaction (1) will be quite undetectable. It will be shown, however, that reaction (2), on the other hand, can take place very rapidly.

The interaction of a hydrogen atom with a hydrogen molecule requires an energy of activation of about 7 kcal. (page 206), and the activation energy for reaction (2) is probably very small compared with this value, since at large distances the molecule is attracted by polarization forces to the ion and this attraction may persist to small distances between the molecule and ion. In these circumstances the separation of the reacting species at the activated state will be large, so that both of the reactants may be considered to rotate as freely as when they are completely separated. The conditions are similar to those arising in the combination of free radicals (page 131), and the apparent activation energy will be the result of the superposition of the centrifugal force of rotation and the attraction due to polarization, acting in opposite directions. The polarization energy, between the molecule and ion, at relatively large distances of separation is given by

$$E_{\text{pol.}} = \frac{\alpha \epsilon^2}{2r^4} \quad (18)$$

and the rotational energy is

$$E_{\text{rot.}} = \frac{J(J+1)h^2}{8\pi^2 m_H r^2}, \quad (19)$$

¹⁵ H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936)

where r is the distance between the centers of the molecule and the ion, α is the polarizability of the hydrogen molecule, m_H is the mass of the hydrogen atom and J is the rotational quantum number. As already shown in Chap. III, the distance between the molecule and ion in the activated state is given by Eq. (45), page 133, and the corresponding activation energy [Eq. (46), page 133] is

$$E = \frac{J^2(J+1)^2 \hbar^4}{128\pi^4 m_H^2 \alpha^2 \varepsilon^2} \quad (20)$$

$$= J^2(J+1)^2 a^2 kT, \quad (21)$$

where a^2 is defined by

$$a^2 = \frac{\hbar^4}{128\pi^4 m_H^2 \alpha^2 \varepsilon^2 kT}. \quad (22)$$

The rate of the reaction can now be written down in terms of the theory of absolute reaction rates. Since the two reactants are relatively far apart in the activated state, the rotational and vibrational degrees of freedom in this state may be taken to be the same as for the isolated molecule and ion. In the reaction-rate equation, therefore, the corresponding partition functions will cancel, and so the partition function for the activated state needs to contain only terms for translation and for the combined rotational and polarization energy. When the rotational number J is zero and the rotational energy is zero, there can be no effective activated state,* it is convenient, therefore, to separate the probability of this state, which is $e^{0/kT}$, i.e., unity, from the remainder of the partition function, and the latter is written as

$$1 + \sum_{J=1}^{\infty} (2J+1) e^{-E/kT}. \quad (23)$$

The rate equation is then

$$k = \kappa \frac{(2\pi m_{H_2} kT)^{3/2}}{h^3} \cdot \frac{(2\pi m_{H_2} kT)^{3/2}}{h^3} \times \left[1 + \sum_{J=1}^{\infty} (2J+1) e^{-E/kT} \right] \frac{kT}{h}. \quad (24)$$

* This is because the only force acting is the attractive force due to polarization, and this would lead to an apparently negative activation energy.

If the value of E given by Eq. (21) is utilized, the quantity in the square brackets may be replaced by A , where

$$A \equiv 1 + \sum_{J=1}^{\infty} (2J+1) e^{-J^2(J+1)^2 a^2} \quad (25)$$

Since the numerical value of a^2 is small, *viz.*, $2.76 \times 10^{-3}/T$, the summation A may be replaced by an integral, thus,

$$A = \int_0^{\infty} (2J+1) e^{-J^2(J+1)^2 a^2} dJ = \frac{\pi^{1/2}}{2a} \quad (26)$$

$$\frac{(2\pi\alpha kT)^{1/2} 4\pi^2 m_H \varepsilon}{h^2}; \quad (27)$$

and if this value is inserted in Eq. (24), the result is

$$k = \kappa \left(\frac{m_{H_4^+}}{m_{H_2} m_{H_2^+}} \right)^{3/2} 2\pi m_H \alpha^{1/2} \varepsilon. \quad (28)$$

Upon assuming the transmission coefficient to be unity and inserting the known values of the masses and the polarizability of the hydrogen molecule, it is found that

$$\begin{aligned} k &= 2.07 \times 10^{-9} \text{ cc. molecule}^{-1} \text{ sec.}^{-1} \\ &= 1.25 \times 10^{15} \text{ cc. mole}^{-1} \text{ sec.}^{-1}, \end{aligned}$$

so that the velocity of the reaction $H_2 + H_2^+ = H_3^+ + H$ should be very high.

HYDROGEN-HALOGEN REACTIONS¹⁶

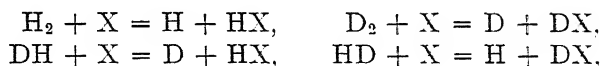
Three-electron Problem.—The equations on which the potential-energy calculations in Chap. III were based involved the assumption that *s*-electrons only were concerned in the reaction. For such electrons the form of the eigenfunction, which gives the electron distribution about the nucleus of the atom, is symmetrical, and the question of directed valence does not arise. For a *p*-, or higher, electron, however, the eigenfunction is no longer symmetrical, and the situation is not so simple. By applying the Heitler-London method of calculating the first-order perturbation energy between H and HCl, considered as a three-electron problem with two *s*- and one *p*-electron, it has been found that the activated state having the lowest potential energy is not linear, as would be the case for three *s*-electrons,

¹⁶ A. Wheeler, B. Topley and H. Eyring, *ibid.*, **4**, 178 (1936).

but triangular.¹⁷ In fact the results imply that a structure of this type, with the formula H_2Cl , should be stable with respect to $\text{H}_2 + \text{Cl}$.

It must be pointed out that the results of calculations of the Heitler-London type are at best approximate, as is evident from the values obtained for the dissociation energy of hydrogen (page 82), and so it is not known how much importance can be attached to the conclusions mentioned above. In view of the arduous nature of the computations, it would seem worth while, for the present, to see what results may be obtained by treating a system of two *s*- and one *p*-electron as one of three *s*-electrons, forming a linear activated complex, and applying the semi-empirical method described in Chap. III.

The reactions involving a molecule of hydrogen and a halogen atom, *viz.*,



X being a halogen, will be considered as three-electron problems, with a linear complex of the form depicted in Fig. 55, where

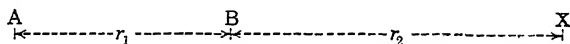


Fig. 55.—System of a hydrogen, deuterium, or hydrogen deuteride molecule (AB) and a halogen atom (X).

A and B are hydrogen or deuterium atoms. The potential-energy surface, which is the same for all four reactions with any one halogen, may be plotted from the spectroscopic data for the molecules A_2 or B_2 , *i.e.*, H_2 , and AX or BX , *i.e.*, HX . From the surface the dimensions r_1 and r_2 of the activated state, and hence the moment of inertia, and also the normal vibration frequencies may be found. The results obtained for the energy of activation in various cases are discussed in the following sections; unless otherwise stated the assumption is made that 20 per cent of the binding energy of all the molecules concerned is coulombic (additive) in nature.

Hydrogen-Chlorine Reactions.—The interatomic distances in the activated state are $r_1 = 1.40$ and $r_2 = 1.30$ Å.; they are, of course, independent of the nature of the isotope of hydrogen concerned. The moments of inertia *I* for various hydrogen-

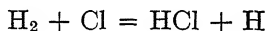
¹⁷ J. L. Magee, *ibid.*, 8, 677 (1940).

chlorine systems, calculated from these dimensions, are given in Table IX, together with the normal vibration frequencies; ν_s is the stretching frequency, and ν_ϕ is the doubly degenerate bending frequency. The frequency ν_i , which has an imaginary value, is also included in case it is required for the application of the correction for penetration of the energy barrier.

TABLE IX.—PROPERTIES OF HYDROGEN-CHLORINE ACTIVATED COMPLEXES

System	$I \times 10^{40}$, g. cm. ²	ν_s , cm. ⁻¹	ν_ϕ , cm. ⁻¹	ν_i , cm. ⁻¹
H-H-Cl	8.55	2,496	551	720 <i>i</i>
H-D-Cl	8.94	1,800	415	705 <i>i</i>
D-H-Cl	15.11	2,496	523	520 <i>i</i>
D-D-Cl	16.33	1,769	386	406 <i>i</i>

The difference in the potential energy of the activated and initial states, *i.e.*, the so-called "classical" activation energy E_c , is found from the potential-energy surface to be 11.6 kcal., and for the determination of E_0 the necessary zero-point energies are obtained from the vibration frequencies of the initial and activated states. For the reaction



the zero-point energies of H_2 and of $\text{H}-\text{H}-\text{Cl}$ are required; these are 6.2 and 5.1 kcal., respectively, and so it follows that

$$E_0 = 11.6 + 5.1 - 6.2 = 10.5 \text{ kcal.}$$

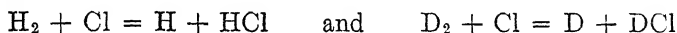
This result may be compared with the experimental value of 6 kcal.¹⁸ By taking a larger proportion of additive energy than the 20 per cent assumed in the above calculations, as would be quite reasonable in view of the fact that the chlorine electron is in a 3*p* state (*cf.* page 84), the theoretical activation energy would be reduced and hence would be in better agreement with that observed.

The specific rate for the process under consideration can be written in the same form as Eq. (1), which is for a reaction of exactly similar general type. The nuclear spin factor i_n is

¹⁸ W. H. Rodebush and W. C. Klingelhoefer, *J. Am. Chem. Soc.*, **55**, 130 (1930); see also J. C. Morris and R. N. Pease, *J. Chem. Phys.*, **3**, 796 (1935).

unity, and the quantity g_{ABC}/g_{AgBC} is assumed also to have this value; the symmetry factors for H_2 and D_2 are 2, but in all other cases they are unity. The transmission coefficient κ is probably close to unity, and it will be assumed to have this value. The vibration frequencies required for the evaluation of the rate constant are known (Table IX) and upon making the approximation that E_c is 7.0 kcal., *i.e.*, E_0 is 5.9 kcal., the calculated specific reaction rate at 298°K. is found to be 7×10^9 , compared with an experimental value of 8×10^9 cc. mole⁻¹ sec.⁻¹. If E_0 is taken as 5.3 kcal., which is in harmony with the temperature variation of the reaction velocity at 1000°K., the calculated rate constant at this temperature is 1.1×10^{13} , and the observed specific rate is 5.5×10^{12} cc. mole⁻¹ sec.⁻¹.¹⁹

By taking E_c to be 7.0 kcal., as before, the relative rates of the reactions



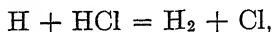
can be derived by using the moments of inertia and vibration frequencies in Table IX; these are 5.6 and 3.3 at 0 and 25°c., respectively. The process in which hydrogen is concerned is faster than that involving deuterium. Measurements have been made of the rate of combination of atomic chlorine with molecular hydrogen and deuterium, in the presence of carbon monoxide and under the influence of light; if it is assumed that the ratio of the rates gives the ratio for the two aforementioned reactions, the experimental values are 13.4 at 0° and 9.75 at 32°c. Although the calculated and observed results are in qualitative agreement, the discrepancy suggests that the frequencies derived for the activated state are too large. A possible explanation of this discrepancy may be found in a consideration of the triangular activated complex as an alternative to the linear one.²⁰ In the former case there would be three degrees of rotational freedom and two of vibration in the activated state, instead of two and three, respectively. Since the rotational is larger than the vibrational partition function, the frequency factor $(kT/h)F^\ddagger/F_i$ would be greater for the triangular than for

¹⁹ Cf. Rodebush and Klingelhoefer, Ref. 18; W. Steiner and E. K. Rideal, *Proc. Roy. Soc.*, **173**, A, 503 (1939); J. C. Morris and R. N. Pease, *J. Am. Chem. Soc.*, **61**, 396 (1939).

²⁰ Magee, Ref. 17.

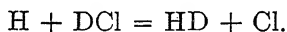
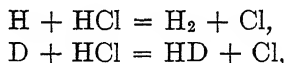
the linear complex; further, the relative increase would be greater the smaller the mass of the hydrogen isotope concerned. The mass dependence of the rate constant is changed from an order of $m^{-3/2}$ to m^{-2} , so that the ratio of the rates with hydrogen and deuterium will be increased. The calculated ratio will thus be in better agreement with experiment.

The activation energy of the reverse reaction, *e.g.*,



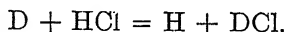
can be obtained directly from the results given above, provided that the heat change in the process is known (*cf.* page 86). For the reaction as written, ΔH is $+1.9$ kcal., and so the calculated energy of activation would be less by this amount than that for the reverse change.

The equation of the theory of absolute reaction rates, of the form of Eq. (1), together with the data in Table IX, may be utilized to calculate the ratio of the rates of the three analogous isotopic reactions



The result obtained in this manner for $k_{\text{H}+\text{HCl}}:k_{\text{D}+\text{HCl}}:k_{\text{H}+\text{DCl}}$ is 1.5:1.1:1.0, whereas the ratio of the experimental rates is 3:1:1.3²¹; it will be noted that there is a considerable discrepancy between the observed and calculated values for the $\text{H} + \text{HCl}$ and $\text{D} + \text{HCl}$ reactions. This is analogous to that noted above in connection with the $\text{H}_2 + \text{Cl}$ and $\text{D}_2 + \text{Cl}$ reactions, in which the same, or similar, activated complexes are involved.

Exchange Reactions.²²—In addition to the reactions just considered, the isotopic forms of hydrogen and hydrogen chloride can take part in the exchange reaction

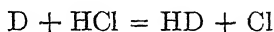


This process involves a different potential-energy surface from that applicable to the other reactions, for the configuration of

²¹ G. K. Rollefson, *J. Chem. Phys.*, **2**, 144 (1934); Steiner and Rideal, *Ref. 19*.

²² Steiner and Rideal, *Ref. 19*.

the activated complex is now $\text{D}-\text{Cl}-\text{H}$, instead of $\text{D}-\text{H}-\text{Cl}$, and the essential parts of this surface, based on 20 per cent additive energy, are shown in Fig. 56. It is seen that, apart from zero-point energies, the activation energy for the exchange reaction is approximately 5 kcal. The corresponding calculated value for the alternative process



is known, from the data already given, to be about 9 kcal.; and so the exchange reaction might be expected to be the more rapid of the two simultaneous reactions taking place between atomic

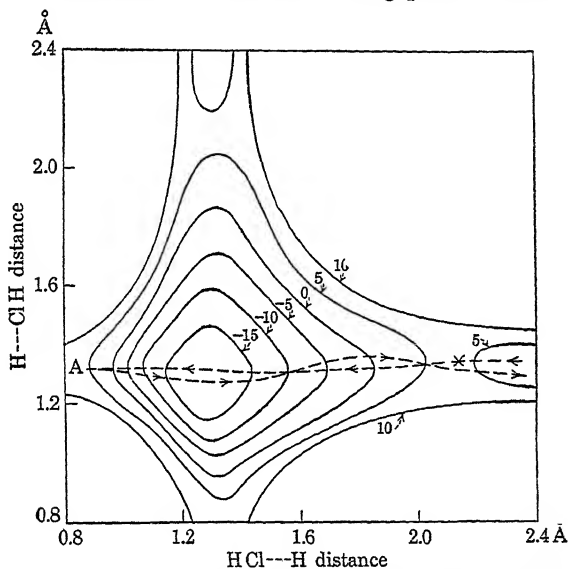
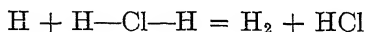


FIG. 56.—Potential-energy surface for the reaction between atomic hydrogen (or deuterium) and hydrogen chloride. (Steiner and Rideal.)

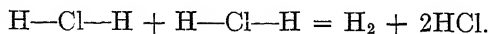
deuterium and hydrogen chloride, especially as the partition functions would also favor the exchange reaction. The experimental results, however, show that this process is actually the slower of the alternative reactions. The explanation of this discrepancy appears to lie in the low transmission coefficient for the exchange reaction. The axes in Fig. 56 are at 90 deg., and this is approximately the correct angle required, according to Eq. (10), page 102, for a point mass sliding on the potential-energy surface to represent the mechanics of the reacting system.

It is seen that the shape of the surface is such that a system possessing mainly relative translational energy coming up the "east-west" valley will be reflected back, as shown in Fig. 56, in the vicinity of *A*. It follows, therefore, that many of the reacting systems which have sufficient energy to pass through the activated state will be returned to their original condition; *i.e.*, the transmission coefficient will be appreciably less than unity. Although the potential-energy surface is probably not exact in the region *A* in which reflection occurs, since the interatomic distances are so small that the semi-empirical method of construction breaks down (*cf.* page 83), it is probable from the general nature of Fig. 56 that the equipotential contour lines are perpendicular to the reaction path shown; this is all that is necessary for the transmission coefficient to be small.

The H—Cl—H Complex.—It was mentioned on page 222 that Heitler-London calculations for two *s*- and one *p*-electrons point to the possibility of a stable triangular complex H—Cl—H (or H—Cl—D). The existence of such a substance might account for the marked effect of hydrogen chloride on the recombination of hydrogen atoms. It is clear, from the shape of the potential-energy surface, that a simple collision between H and HCl will rarely lead to the formation of H—Cl—H unless a third body is present to remove the excess energy; it is suggested, therefore, that the combination occurs as a wall reaction and that the resulting complex is readily desorbed, eventually reacting in the gas phase, thus:

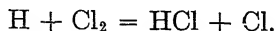


or



In this way, it is possible to account for the accelerating influence of hydrogen chloride on the combination of hydrogen atoms; if this explanation is correct, a pronounced influence of the walls of the reaction vessel should be observed.

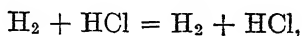
Other Hydrogen-Chlorine Reactions.²³—Approximate calculations have been made of the activation energy of the reaction



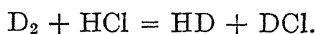
²³ Eyring, Ref. 7; J. C. Morris, unpublished.

On the assumption that 14 per cent of the binding energy is additive, the energy of activation is about 2.7 kcal. No allowance has been made for zero-point energies, but the difference between the values in initial and activated states is, in general, quite small. The experimental activation energy of approximately 2 kcal. is in satisfactory agreement with that calculated.

The potential-energy surface in bond space has been plotted for the exchange reactions of the type

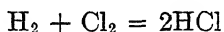


of which an illustration is



On the basis of 17 per cent coulombic energy, the classical activation energy, *i.e.*, zero-point energies being neglected, is found to be 53 kcal.; an alternative calculation, based on 20 per cent additive energy, gives 43.6 kcal. for E_c , and after making the necessary allowances E_0 is found to be 50.6 kcal. for the $\text{H}_2 + \text{HCl}$ reaction and 48.9 kcal. for that between D_2 and HCl . The experimental value for the latter process at 1000°K. is approximately 57 kcal.

The reaction



has been treated in an approximate manner only, the system being regarded as one of four s-electrons. The activation energies based on different assumed proportions of coulombic energy, if the zero-point terms are neglected, are as follows:

Coulombic energy, per cent.....	10	14	20
Activation energy, kcal.....	54	44.5	29.5

All that is known experimentally is that the value is greater than 36 kcal., for this is the energy of activation of the reaction between molecular hydrogen and atomic chlorine (page 238), and it is known that the reaction between hydrogen and chlorine occurs almost exclusively through atoms of the latter.

Hydrogen-Bromine Reactions.²⁴—The reactions between the isotopic forms of molecular hydrogen and atomic bromine may

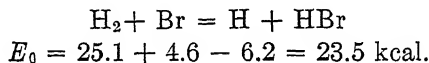
²⁴ Wheeler, Topley and Eyring, Ref. 16.

be treated in a manner exactly analogous to that for the corresponding reactions with chlorine. In the activated state the distance r_1 (from hydrogen to hydrogen) is 1.5 Å.; that of r_2 (from bromine to the adjacent hydrogen) is 1.42 Å. The corresponding moments of inertia and vibrational frequencies are recorded in Table X.

TABLE X.—PROPERTIES OF HYDROGEN-BROMINE ACTIVATED COMPLEXES

System	$I \times 10^{40} \text{g. cm.}^2$	$\nu_s \text{ cm.}^{-1}$	$\nu_\phi \text{ cm.}^{-1}$	$\nu_l \text{ cm.}^{-1}$
H-H-Br	10.34	2,340	460	760 <i>i</i>
H-D-Br	12.15	1,670	350	760 <i>i</i>
D-H-Br	18.43	2,340	430	540 <i>i</i>
D-D-Br	20.19	1,670	320	540 <i>i</i>

From the potential-energy surface, the classical activation energy E_c is found to be 25.1 kcal., on the assumption of 20 per cent coulombic energy, so that for the reaction



where 4.6 kcal. is the zero-point energy of the activated state, calculated from ν and ν_ϕ (doubly degenerate) in Table X. The experimental energy of activation is about 18 kcal.²⁵; the difference is quite appreciable, but better agreement would have been obtained by assuming a higher proportion of additive energy or by basing the calculations on a triangular, instead of a linear, structure for the activated complex.

Taking E_c as 20.5 kcal., in order to be in agreement with experiment at 574.5°K., the results in Table XI have been calculated by means of the appropriate form of the statistical equation for the rate constant. The ratio of the rates for the reaction involving hydrogen and deuterium, respectively, assuming the same classical activation energy, are also given.

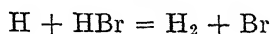
As before, the calculated ratios k_H/k_D are too low; but they would be improved, as explained above, if the activated complex were triangular instead of linear.

²⁵ M. Bodenstein and H. Lütke Meyer, *Z. physik. Chem.*, **114**, 208 (1924); F. Bach, K. F. Bonhoeffer and E. A. Moelwyn-Hughes, *ibid.*, **B**, **27**, 71 (1934); see also Morris and Pease, Ref. 18.

TABLE XI.—CALCULATED AND OBSERVED SPECIFIC REACTION RATES

Specific rate	499°K.		574.5°K.		612°K.	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$k(\text{H}_2 + \text{Br})$	1.16×10^6	1.01×10^6	(1.25×10^7)		3.01×10^7	3.46×10^7
$\frac{k(\text{H}_2 + \text{Br})}{k(\text{D}_2 + \text{Br})}$	7.1	4.2	5.4	2.9	4.8	2.5

The value of ΔH for the reverse reaction



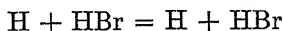
is 16.4 kcal., and so the activation energy must be of the order of 4 kcal. or less; experimental data indicate that the value is actually quite small. By assuming it to be zero and employing the data in Table X in the rate equation based on the theory of absolute reaction rates, the specific rate constants are calculated to be 3.6×10^{13} and 4.5×10^{13} at 500 and 900°K., respectively, and the experimental results are 1.3×10^{13} and 2.5×10^{13} cc. mole⁻¹ sec.⁻¹. If E_0 were taken as 1 kcal. the agreement would be almost exact.

Approximate energies of activation have been derived for other hydrogen-bromine reactions; these are given in Table XII, where they may be compared with the experimental results.²⁶ The values in the columns headed I, II and III are based on the assumption of 10, 14 and 20 per cent coulombic energy, respectively.

TABLE XII.—CALCULATED AND OBSERVED ACTIVATION ENERGIES

Reaction	Obs., kcal.	Calc., kcal.		
		I	II	III
$\text{H} + \text{Br}_2 = \text{HBr} + \text{Br}$	1.2	3	2.1
$\text{H}_2 + \text{Br}_2 = 2\text{HBr}$	>43	45	39	26.5

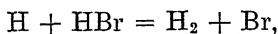
Exchange Reactions.²⁷—The potential-energy surface for the exchange reaction



²⁶ Morris and Pease, Ref. 18.

²⁷ W. Steiner, *Proc. Roy. Soc.*, **173**, A, 531 (1939).

involving the activated complex $\text{H}-\text{Br}-\text{H}$, or $\text{D}-\text{Br}-\text{H}$, on the assumption of 20 per cent coulombic energy, is shown in Fig. 57; the activation energy of the reaction is seen to be about 3 kcal. Since the energy of activation of the reverse process just considered, *i.e.*,



is almost zero, the latter might be expected to be faster, whereas the reverse is true in the reaction between deuterium and hydrogen bromide. This result appears to be due to the very low

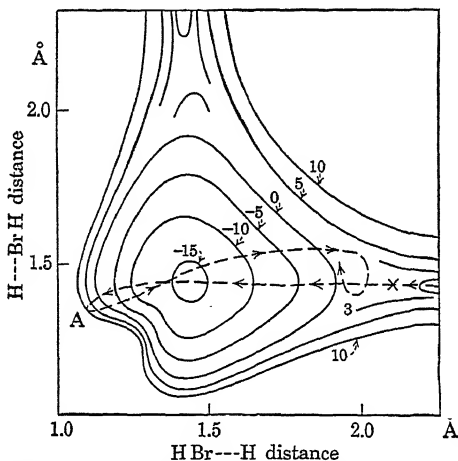
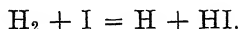


FIG. 57.—Potential-energy surface for the reaction between atomic hydrogen (or deuterium) and hydrogen bromide. (Steiner.)

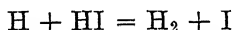
value of the bending frequency of the activated complex $\text{D}-\text{Br}-\text{H}$, *viz.*, 70 cm^{-1} , compared with 480 cm^{-1} for the analogous frequency of the $\text{D}-\text{H}-\text{Br}$ complex (Table X); the ratio of the partition functions, as a consequence of this difference, leads to a factor of 10 in favor of the exchange reaction. The physical significance of the low bending frequency of $\text{D}-\text{Br}-\text{H}$ and the correspondingly high partition function is that there is a considerable probability of forming the activated state even when the line of the approaching deuterium atom makes an appreciable angle with the direction of the axis of the molecule; with the $\text{D}-\text{H}-\text{Br}$ complex, however, the atom must approach very nearly along the line of centers if the activated state is to be formed.

Attention may be called to the difference in behavior between chlorine and bromine in connection with the reactions under discussion; in the latter case the exchange process is the more rapid, whereas in the former the alternative reaction, leading to molecular hydrogen or hydrogen deuteride, is the faster. Part, at least, of the difference can be attributed to the respective transmission coefficients, as may be seen by comparing Figs. 56 and 57. In the region *A*, where a system approaching along the bottom of the "east-west" valley is liable to be reflected, the equipotential lines in the case of the bromine reaction are not perpendicular to the "east-west" valley, as they are for the reaction with chlorine. The mass point representing the reacting system will thus be trapped in the potential-energy basin at the top of the pass between the two valleys, as indicated by the dotted line in Fig. 57, and the transmission coefficient will be determined by the same considerations as were discussed in connection with the hydrogen atom-molecule reactions on page 207. For the symmetrical reaction $\text{H} + \text{HBr} = \text{H} + \text{HBr}$, the value of κ is clearly 0.5; for the exchange reaction $\text{D} + \text{HBr} = \text{H} + \text{DBr}$ the gaps in the basin are at slightly different levels and the transmission coefficient will differ slightly from this value, but it will never be so small as for the corresponding reaction with chlorine.

Hydrogen-Iodine Reactions.²⁸—Later, it will be seen that interaction between hydrogen and iodine does not involve iodine atoms; there is therefore no object in making at this point a detailed calculation of the activation energy of the reaction



The approximate results for this process and for the reaction between atomic hydrogen and molecular iodine are given in Table XIII. The figures for the reaction



are based on a ΔH value of 32.7 kcal. The results in the columns headed I and II involve 10 and 14 per cent coulombic energy, respectively.

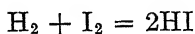
²⁸ Wheeler, Topley and Eyring, Ref. 16.

TABLE XIII.—CALCULATED AND OBSERVED ACTIVATION ENERGIES

Reaction	Obs., kcal.	Calc., kcal.	
		I	II
$\text{H}_2 + \text{I} = \text{H} + \text{HI}$	34.2	43.3	40.4
$\text{H} + \text{HI} = \text{H}_2 + \text{I}$	1.5	10.6	7.7
$\text{H} + \text{I}_2 = \text{HI} + \text{I}$	0	2.5	1.8

It must be admitted that the agreement is not always good, but the calculated values are at least qualitatively correct.

The reaction



has been treated in some detail as a four-electron problem, the question of directed valence of the iodine being neglected; this would probably introduce an error of not more than about 5 kcal. As seen on page 126, the six normal vibration frequencies can be divided into three groups as follows:*

System	I	II			III	
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
$\text{H}_2 + \text{I}_2$	994	86	1,280	965 <i>i</i>	1,400	1,730
$\text{D}_2 + \text{I}_2$	700	86	915	678 <i>i</i>	990	1,225

The activated state is presumably planar and symmetrical with respect to the *LM* plane (see Fig. 32, page 126), and hence three interatomic distances are sufficient to give the required configuration; these are $\text{H}-\text{H} = 0.97 \text{ \AA.}$, $\text{H}-\text{I} = 1.75 \text{ \AA.}$ and $\text{I}-\text{I} = 2.95 \text{ \AA.}$ The three moments of inertia of the activated complex are

Complex	$A \times 10^{40} \text{ g.cm.}^2$	$B \times 10^{40} \text{ g.cm.}^2$	$C \times 10^{40} \text{ g.cm.}^2$
$\text{H}_2 \text{ I}_2$	921.5	6.9	928.4
$\text{D}_2 \text{ I}_2$	922.2	13.8	935.7

* The value of *a* used in the Morse equation for HI, on which the calculations of vibration frequencies were based, is somewhat in error; the effect on the results recorded is, however, relatively small.

and the values for H_2 , D_2 and I_2 are 0.456, 0.913 and 748.5×10^{-40} g.cm.², respectively. The classical activation energy, on the assumption that 14 per cent of the binding energy of the diatomic molecules is additive, is found to be 48.3 kcal. For the reaction between H_2 and I_2 , therefore,

$$E_0 = 48.3 + 7.8 - 6.5 = 49.6 \text{ kcal.},$$

the zero-point energy of the activated state being 7.8 kcal. and that of the reactants 6.5 kcal., *i.e.*, 6.2 for H_2 and 0.3 for I_2 . For the reaction with deuterium, the corresponding zero-point energies are 5.6 and 4.7 kcal, respectively; hence,

$$E_0 = 48.3 + 5.6 - 4.7 = 49.2 \text{ kcal.}$$

It will be noted that in both instances the zero-point energy is apparently greater in the activated state than in the initial state; this result is somewhat surprising and would imply an error in the potential-energy surface leading to an incorrect assignment of vibration frequencies. This error may also account for the high values of the activation energy compared with the experimental result of 40 kcal.²⁹ The formula for the specific rate constant, based on the theory of absolute reaction rates, omitting the factor for leakage through the barrier, is

$$k = \kappa \frac{\frac{(2\pi m_{\ddagger} kT)^{3/2}}{h^3}}{\frac{(2\pi m_1 kT)^{3/2}}{h^3} \cdot \frac{(2\pi m_2 kT)^{3/2}}{h^3}} \cdot \frac{\frac{8\pi^2(8\pi^3 ABC)^{1/2}(kT)^{3/2}}{h^3 \sigma_{\ddagger}}}{\frac{8\pi^2 I_1 kT}{h^2 \sigma_1} \frac{8\pi^2 I_2 kT}{h^2 \sigma_2}} \cdot \frac{\prod (1 - e^{-h\nu_{\ddagger}/kT})}{(1 - e^{-h\nu_1/kT})^{-1}(1 - e^{-h\nu_2/kT})^{-1}} \cdot \frac{kT}{h} e^{-E_0/RT}, \quad (29)$$

where the numerator refers to the activated complex and the denominator to the reactants; the suffix \ddagger is used for the activated state, and 1 and 2 are used for hydrogen and iodine molecules, respectively. The symmetry number σ_{\ddagger} is 4, whereas σ_1 and σ_2 are each 2, and so their resultant is unity. The nuclear spin factor is omitted since there is no change in the ortho-para ratio,

²⁹ M. Bodenstein, *Z. physik. Chem.*, **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1898); cf. W. C. McC. Lewis, *J. Chem. Soc.*, **113**, 471 (1918); see also L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," p. 154, Chemical Catalog Co., Inc., 1932; C. N. Hinshelwood, "Kinetics of Chemical Change," Oxford University Press, 4th ed., p. 100, 1940.

and the electronic factor is also taken as unity. Since the calculated frequencies are known to be in error, there is little purpose in testing Eq. (29) by means of them; but some indication of the value of the results may be obtained by taking the frequencies ν_5 and ν_6 to be 180 and 1,000 cm^{-1} and leaving the others unchanged. The observed reaction velocity at 700°K. requires E_0 to be 39.7 kcal., and by use of this figure and the modified vibration frequencies the reaction rate constants at 575 and 781°K. have been calculated; the results are compared with the experimental data in Table XIV.

TABLE XIV.—CALCULATED AND OBSERVED RATES OF THE $\text{H}_2\text{-I}_2$ REACTION

$T, ^\circ\text{K.}$	Obs.	$\log k$	Calc.
575	-0.88	-0.85
700	(1.808)
781	3.13	3.09

It must be admitted that the agreement obtained in this way is somewhat artificial, but it shows that with reasonable assumptions the method described for the calculation of the absolute rates of reactions is capable of yielding satisfactory results.

Hydrogen-Fluorine Reactions.³⁰—Approximate activation energies have been calculated by the semi-empirical method for reactions between hydrogen and fluorine. The results are summarized in Table XV; the values in columns I and II are based on 10 and 14 per cent coulombic energy, respectively.

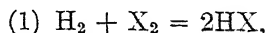
TABLE XV.—CALCULATED AND OBSERVED ACTIVATION ENERGIES

Reaction	Obs., kcal.	Calc., kcal.	
		I	II
$\text{H} + \text{F}_2 = \text{HF} + \text{F}$..	5.1	3.3
$\text{H}_2 + \text{F} = \text{HF} + \text{H}$	8	10.6	6.3
$\text{H}_2 + \text{F}_2 = 2\text{HF}$	>25	50.0	...

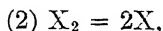
Little is known from direct observation concerning the energy of activation of the reaction between hydrogen and fluorine; it can be said definitely, however, that it is large.

³⁰ Eyring, Ref. 7.

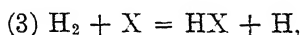
Discussion of Results of Hydrogen-Halogen Reactions.—An interesting application of the results derived above is to determine whether the over-all reaction represented by



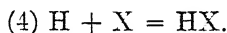
where X is a halogen, takes place through the molecular halogen or whether the atoms are involved; the alternative possibility is primary dissociation,



followed by



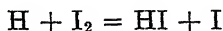
and



The last of these steps, involving the combination of two atoms, will have a very small, or zero, activation energy (page 131); and, provided that the excess energy is removed in a three-body collision, this need not be discussed further in relation to the rate-determining step. Consider the reaction between hydrogen and iodine; the activation energy for the molecular reaction (E_1) is calculated to be approximately 48 kcal., and for that involving iodine atoms (E_3) it is about 40 kcal. To determine which of the two processes will predominate, it is necessary to assume that a stationary state is soon attained in which the iodine molecules and atoms are in equilibrium (*cf.* page 212); the dissociation energy per gram-atom of iodine, *i.e.*, 17 kcal., must then be added to E_3 to get the *effective* energy of activation for the reaction with iodine atoms when the initial material is molecular iodine. It follows, therefore, that

$$E_{\text{atomic}} = 40 + 17 = 57 \text{ kcal.}$$

The activation energy for the process involving atomic iodine is thus appreciably greater than that in which molecular iodine reacts directly with the hydrogen, and so it is evident that mechanism (1) is the correct one. It is of interest to note that since the reaction



has an activation energy of almost zero (Table XIII) the reaction between *hydrogen* atoms and iodine molecules would require an

effective activation energy of only 51.5 kcal., *i.e.*, the dissociation energy per gram-atom of hydrogen. In this particular case, therefore, it would be easier for the hydrogen-halogen reaction to take place via hydrogen atoms than via halogen atoms.

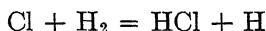
For the hydrogen-bromine reaction the activation energy for the reaction involving bromine atoms is

$$E_{\text{atomic}} = 18 + 22.6 = 40.6 \text{ kcal.},$$

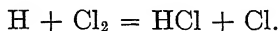
the heat of dissociation of 1 mole of bromine being 45.2 kcal., so that the energy of dissociation per gram-atom is 22.6 kcal. The calculated activation energy for the molecular reaction (E_1) and E_{atomic} are not very different, and hence the molecular and atomic reactions might be expected to occur simultaneously. It is found in practice that the reaction via bromine atoms predominates.

The activation energies for the alternative reactions with chlorine are 54 or 45 kcal. for E_1 , based on 10 or 14 per cent coulombic energy, respectively, whereas E_{atomic} is approximately $7 + \frac{1}{2} \times 56.8$, *i.e.*, about 36 kcal. In this instance the atomic reaction should undoubtedly occur in preference to that involving molecular chlorine, and that this is actually the case is evident from the accepted mechanism for the photochemical hydrogen-chlorine reaction.

It is generally agreed that, following the primary dissociation of chlorine molecules into atoms by the absorbed light, a chain reaction occurs in which the successive stages are

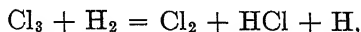


and



The activation energy of the second step is about 2 kcal. (page 229), and so it is evident that the first stage must be rate-determining. The activation energy of this reaction has been calculated to be about 10 kcal., but the actual value is probably somewhat lower (see page 224).

It was noted on page 134 that there is evidence for the existence of a relatively stable Cl_3 molecule, and the question of its participation as a chain carrier by means of the reaction



as an alternative to the stage involving atomic chlorine, must be considered.³¹ The Cl_3 molecule is probably linear like the metastable molecule H_3 , and so a possible configuration of the activated state for the foregoing reaction is as shown in Fig. 58. The energy in excess of that of the separated molecules was found to be 31 kcal., on the assumption that 10 per cent of the binding energy of the diatomic molecules is additive; if this result is compared with those already given for the reaction between hydrogen and atomic chlorine, it would seem that Cl_3 molecules are unlikely to act as chain carriers. It may be noted, however, that if the dimensions in the $\text{Cl}-\text{Cl}-\text{Cl}-\text{H}-\text{H}$ complex were changed somewhat, *e.g.*, if the $\text{Cl}-\text{H}$ distance were taken to be 1.45 Å. and the $\text{H}-\text{H}$ distance 0.90 Å., the activation energy for the reaction between Cl_3 and H_2 would be lowered to

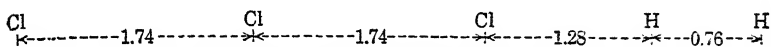
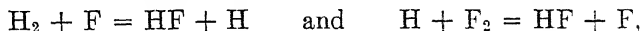


FIG. 58.—Possible dimensions of linear activated state in the reaction between triatomic chlorine and a hydrogen molecule.

20.5 kcal. It is not impossible that the Cl_3 complex may play a part in the photochemical hydrogen-chlorine reaction, and mechanisms involving this substance have been proposed; there does not, however, appear to be a unanimous opinion on this matter.

The calculated activation energy of the reaction between molecular hydrogen and molecular fluorine is 50 kcal., and so the reaction between H_2 and F_2 will not occur at ordinary temperatures. The reactions involving hydrogen or fluorine atoms, *viz.*,

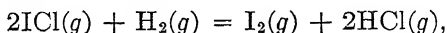


require almost no activation energy; but starting from the molecular species the effective values would be approximately equal to half the heat of dissociation of fluorine or of hydrogen, respectively, *i.e.*, about 40 or 50 kcal., respectively. It seems, therefore, that the reaction between hydrogen and fluorine should be very slow at ordinary temperatures, although a chain reaction might be expected if hydrogen or fluorine atoms were formed to any extent. In view of the marked reactivity of fluorine in other connections, this conclusion appears somewhat surprising; it has been found, nevertheless, that gaseous hydrogen and fluorine

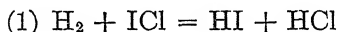
³¹ G. E. Kimball and H. Eyring, *J. Am. Chem. Soc.*, **54**, 3876 (1932).

can be mixed at ordinary temperatures and allowed to stand for appreciable periods without reaction occurring. After several minutes, explosions frequently result; these may be attributed to catalytic influences which lead to local heating, and hence sufficient amounts of atoms may be formed to permit a chain reaction to occur.³²

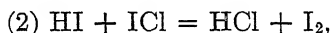
The Hydrogen-Iodine-Monochloride Reaction.—The reaction between hydrogen and gaseous iodine monochloride,



undoubtedly takes place in stages; the following have been suggested



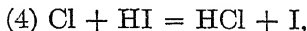
and



the first being slow and the second rapid. The measured heat of activation, 34 kcal., is consequently attributed to the first stage.³³ Approximate treatment of the two partial reactions as four-electron systems has led to the calculated activation energies of 39 and 41 kcal., respectively, on the assumption of 14 per cent coulombic energy. Although these results are by no means exact, they imply that both stages take place with comparable velocities. It appears probable that the second reaction actually occurs in stages, *viz.*,



and



the iodine atoms resulting from the equilibrium $\text{I}_2 \rightleftharpoons 2\text{I}$. The potential-energy calculations show that, of these steps, reaction (3) is the slowest, the activation energy being about 16 kcal. If to this is added 17 kcal., *i.e.*, half the heat of dissociation of molecular iodine, the effective energy of activation of reaction (2) by the two-stage mechanism becomes $17 + 16 = 33$ kcal. Although this is still not very different from that required for the first stage of the reaction, it is nevertheless sufficient to make

³² H. Eyring and L. S. Kassel, *ibid.*, **55**, 2796 (1933).

³³ W. D. Bonner, W. J. Gore and D. M. Yost, *ibid.*, **57**, 2723 (1935).

the over-all stage (2) more rapid than (1). If k_1 and k_2 are the specific rate constants and E_1 and E_2 are the effective activation energies, then

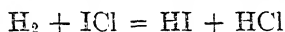
$$\frac{k_2}{k_1} = e^{-(E_2-E_1)/RT}, \quad (30)$$

on the assumption that the frequency factors for the two bimolecular reactions are the same. In the present instance, $E_2 - E_1$ would be about 5 kcal., and hence at 500°K. the ratio of the two rates would be

$$\frac{k_2}{k_1} = e^{5,000/1,000} \approx 150,$$

so that the second stage, according to the foregoing calculations, may be expected to be about 150 times as fast as the first.

A detailed theoretical study³⁴ of the reaction



has been made by plotting the potential-energy surface in bond space (page 121); the calculations were carried out for both 17 and 20 per cent additive binding energy, with the results given below. The dimensions and moments of inertia found for the activated state are given in Table XVI.

TABLE XVI.—DIMENSIONS AND MOMENTS OF INERTIA OF ACTIVATED COMPLEX

Additive energy, per cent	H—H r_1 , Å.	I—Cl r_2 , Å.	H—Cl r_3 , Å.	H—I r_4 , Å.	H—Cl r_5 , Å.	H—I r_6 , Å.	A $\times 10^{40}$ g. cm. ²	B $\times 10^{40}$ g. cm. ²	C $\times 10^{40}$ g. cm. ²
17	0.803	2.34	1.60	2.26	2.21	2.48	254.9	7.7	264.6
20	0.791	2.35	1.56	2.37	2.17	2.55	264.2	10.0	274.2

The values of the six normal frequencies, five real and one imaginary, were obtained by the method described on page 125; these together with the classical activation energy E_c and the value E_0 , after allowing for the zero-point energies, are recorded in Table XVII.

³⁴ W. Altar and H. Eyring, *J. Chem. Phys.*, **4**, 661 (1936); A. Sherman and N. Li, *J. Am. Chem. Soc.*, **58**, 690 (1936).

TABLE XVII.—NORMAL VIBRATION FREQUENCIES AND ACTIVATION ENERGIES

Additive energy, per cent	ν_1 cm. ⁻¹	ν_2 cm. ⁻¹	ν_3 cm. ⁻¹	ν_4 cm. ⁻¹	ν_5 cm. ⁻¹	ν_6 cm. ⁻¹	E_c kcal.	E_0 kcal.
17	4,391	1,580	1,426	481	435	1,128 _i	32.8	37.9
20	4,696	1,522	1,344	550	442	933 _i	24.9	30.3

The activation energies for the experimental temperature (500°K.) may be calculated by the method given on page 195; these are 36.6 and 29.0 kcal., respectively. If, as previously considered, the slow stage in the reaction between hydrogen and gaseous iodine monochloride is the reaction under consideration, then the experimental activation energy, about 34 kcal., is in satisfactory agreement with the result of the semi-empirical potential-energy calculations.

The rate constant for the reaction between H_2 and ICl may be written in the same form as Eq. (29), where the suffixes 1 and 2 refer to H_2 and ICl , respectively; this may be reduced to

$$k = \kappa \left(\frac{m_+}{m_1 m_2} \right)^{3/2} \cdot \frac{\sigma_1 \sigma_2}{\sigma_+} \cdot \frac{(ABC)^{1/2}}{I_1 I_2} \cdot \frac{h^3}{8\pi^2 kT} \cdot \frac{\prod_5 (1 - e^{-h\nu_+/kT})^{-1}}{(1 - e^{-h\nu_1/kT})^{-1} (1 - e^{-h\nu_2/kT})^{-1}} e^{-E_0/RT}. \quad (31)$$

The values of the frequency factor A , derived from Eq. (31) and the calculated activation energies, which satisfy the equation

$$k = A e^{-E/RT} \text{ cc. mole}^{-1} \text{ sec.}^{-1}, \quad (32)$$

are given in Table XVIII, together with those based on the measured rate constants and activation energy.

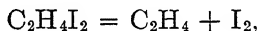
TABLE XVIII.—CALCULATED AND OBSERVED FREQUENCY FACTORS

Temp., °K.	$A_{\text{obs.}}$	$A_{\text{calc.}}$	
		$E = 36.6 \text{ kcal.}$	$E = 29.0 \text{ kcal.}$
478	1.64×10^{15}	4.11×10^{12}	4.30×10^{12}
503	1.49×10^{15}	4.16×10^{12}	4.17×10^{12}
513	1.60×10^{15}	4.09×10^{12}	4.21×10^{12}

From these results, it would appear that the calculated rate constants are too small by a factor of approximately 350; this discrepancy may be due to an error in the vibration frequencies recorded in Table XVII. If the lowest figures were reduced still further, it is possible to improve the agreement between the observed and calculated A factors without appreciably altering the activation energy. It is important to remember, however, that the experimental data for A and E are based on a study of the reaction between hydrogen and iodine monochloride to give iodine and hydrogen chloride, the assumption being made that the rate measured is that of the reaction leading to the formation of hydrogen iodide and hydrogen chloride. Since the two stages in the over-all reaction may well be taking place at rates of the same order of magnitude, it is not certain that the measured quantities may be applied directly to the reaction being discussed and for which the calculations were made.

HYDROCARBON-HALOGEN REACTIONS

Ethylene-Halogen Reactions.³⁵—Processes in which a halogen molecule is added to, or removed from, a double bond, *e.g.*, as in the decomposition of ethylene iodide

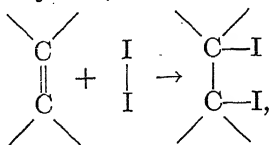


are of importance; a number of them have been studied experimentally and have presented some interesting problems in reaction kinetics. In order to determine the activation energy of the ethylene iodide decomposition reaction, it is more convenient to consider that of the reverse process, *i.e.*, the addition of an iodine molecule to a double bond. If E_1 is the activation energy of the direct reaction and E_2 that of the reverse process, then the difference is equal to the heat of reaction (page 8), the activation energy being greater in the endothermic direction. If direct thermochemical data of the heat of reaction are not available, an approximate figure can be derived by using a set of consistent bond strengths.

The reaction between ethylene and iodine may be considered in the simplified form of the addition of an iodine molecule to a

³⁵ A. Sherman and C. E. Sun, *ibid.*, **56**, 1096 (1934); A. Sherman, O. T. Quimby and O. Sutherland, *J. Chem. Phys.*, **4**, 732 (1936).

double-bonded carbon system, thus,



so that the problem may be considered as one involving four electrons; for the sake of simplicity, and as an approximation, they will be treated as *s*-electrons, having no directional properties. The two carbon atoms remain bound throughout the reaction, but at the commencement they are held by a double bond whereas at the end a single linkage binds them together. The interatomic distance must, therefore, change during the course of the reaction; in order to simplify the calculations the assumption is made that the carbon atoms remain at a constant distance of 1.46 Å. apart: this is taken as being roughly the mean between the single- and double-bond distances. If this is the approximate distance between the carbon atoms in the

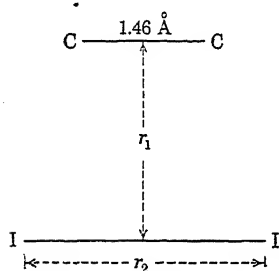


FIG. 59.—Addition of iodine molecule to a double-bonded carbon system.

activated state, there will be no appreciable error in the activation energy, although the potential-energy surface may be somewhat incorrect at other points. The iodine molecule is now supposed to approach the C—C bond symmetrically in the plane of the carbon atoms, as shown in Fig. 59. At the beginning, r_2 is the normal interatomic distance in molecular iodine, taken as 2.66 Å., and r_1 is large; in the course of the reaction, r_1 , which is the perpendicular distance between the C—C and I—I bonds, decreases until the C—I distance becomes the normal value for a C—I bond, taken as 2.10 Å., while at the same time r_2 increases to 2.86 Å. By making the simplifications postulated above, it is possible to express the potential-energy changes of the four-electron system in terms of the two parameters, *viz.*, r_1 and r_2 , only. The potential-energy surface for the reaction can thus be drawn and the activated state identified in the usual manner.

The activation energy obtained for the reaction being considered, assumed to be equivalent to the ethylene-iodine reaction,

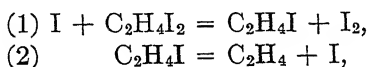
is given in Table XIX under the heading of E_2 ; the value for the reverse process, *i.e.*, the decomposition of ethylene iodide into ethylene and molecular iodine, obtained from E_2 by adding the heat of reaction, is given under E_1 . Calculations, similar to those just described, have been made for the addition of molecular bromine and chlorine to a double bond, and the corresponding activation energies are also recorded in Table XIX. In all cases, the coulombic energy is assumed to be 14 per cent of the total binding energy of the C—C and C—X linkages, X representing a halogen; the constants for the Morse equation were derived from spectroscopic data concerning these bonds.

TABLE XIX.—ACTIVATION ENERGIES OF ETHYLENE-HALOGEN REACTIONS

Reaction	E_1 , kcal.	E_2 , kcal.
$\text{C}_2\text{H}_4\text{I}_2 = \text{C}_2\text{H}_4 + \text{I}_2$	30.0(36)	22.4
$\text{C}_2\text{H}_4\text{Br}_2 = \text{C}_2\text{H}_4 + \text{Br}_2$	50.2	24.4(30)
$\text{C}_2\text{H}_4\text{Cl}_2 = \text{C}_2\text{H}_4 + \text{Cl}_2$	80.4	25.2

The two results in parentheses are approximate experimental values; the agreement is seen to be quite fair, and it could be artificially improved by changing the proportion of additive energy.

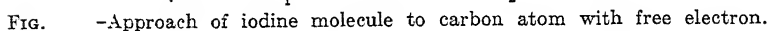
Catalysis by Halogen Atoms.³⁶—In addition to the direct decomposition of ethylene iodide already discussed, it is known that a catalyzed reaction involving iodine atoms also plays an important part, and it is of interest to consider this process. The iodine atoms are formed by the dissociation of the molecules, and then follow the stages



in which the ethylene iodide is decomposed and the iodine atoms are regenerated. The second of these reactions is assumed to be so rapid that the activation energy of the first determines the rate of the catalytic decomposition. The effective or over-all activation energy of the process is obtained by adding half the heat of dissociation of molecular iodine to the activation energy of the rate-determining stage, as is the case in the hydrogen-

³⁶ Sherman and Sun, Ref. 35; Sherman, Quimby and Sutherland, Ref. 35.

be regarded as $\text{CH}_2\text{I}^+\text{CH}_2$ with a free electron on the second carbon atom; then the reaction with molecular iodine becomes essentially a three-electron problem. The iodine molecule may be considered to approach the carbon atom along the line joining the iodine nuclei as shown in Fig. 60. At the commencement, r_2 is the normal I—I distance, and r_1 is large; but as the reaction proceeds, r_1 approaches the single bonded C—I distance



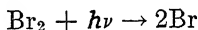
and r_2 becomes large. The potential-energy surface can be drawn and the activation energy derived in the usual manner, by employing the semi-empirical procedure with 14 per cent of the binding energy assumed to be additive. The activation energy for the forward reaction as written (E_1) and for the reverse (E_2) are quoted in Table XX, together with the values for the corresponding processes involving bromine and chlorine. The *effective* activation energies for atomic reactions, obtained by adding half the heat of dissociation of the halogen molecule to E_2 in each case, are given in the column E_a .

Reaction	E_1 , kcal.	E_2 , kcal.	E_a , kcal.
$\text{C}_2\text{H}_4\text{I} + \text{I}_2 = \text{C}_2\text{H}_4\text{I}_2 + \text{I}$	1.8	10.4	28.0(30)
$\text{C}_2\text{H}_4\text{Br} + \text{Br}_2 = \text{C}_2\text{H}_4\text{Br}_2 + \text{Br}$	2.3	22.4	45.0
$\text{C}_2\text{H}_4\text{Cl} + \text{Cl}_2 = \text{C}_2\text{H}_4\text{Cl}_2 + \text{Cl}$	3.0	24.6	53.0

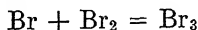
By examining the results in Tables XIX and XX, it is possible to foretell in any particular case whether the decomposition of the ethylene halide will occur by the unimolecular mechanism, *i.e.*, the direct decomposition, for which the activation energy

is given by E_1 in Table XIX, or whether the catalytic decomposition by halogen atoms, for which the activation energy is E_a in Table XX, will predominate. In the case of ethylene iodide, the two calculated activation energies, *viz.*, 30.0 and 28.0 kcal., respectively, are so close that the two mechanisms would be expected to occur simultaneously in the same temperature region; this anticipation is borne out by experiment. For the decomposition of ethylene bromide, it is not possible to predict the course of the reaction exactly. The activation energy calculated for the catalytic decomposition is 45 kcal., compared with 50 kcal. for the unimolecular decomposition, and so the former may be expected to take preference; it is not impossible, however, that both types of decomposition may occur side by side. The situation is more definite with ethylene chloride; here the activation energy for the catalyzed reaction is 53 kcal., as against 80 kcal. for the unimolecular decomposition. It is evident, therefore, that the former mechanism should predominate. In view of the relatively high activation energy, the reaction will have a measurable velocity only if the temperature is at least 700°K. It may be concluded from the results in Tables XIX and XX that ethylene bromide will have an appreciable rate of decomposition at a lower temperature and the iodide at a still lower temperature, as is found to be the case in practice.

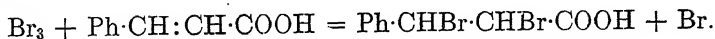
Addition of Triatomic Halogen to Double Bond.³⁷—The suggestion has been made that the photobromination of cinnamic acid in carbon tetrachloride solution takes place in the following manner: the primary photochemical step



is followed by the thermal reactions



and



Some indication of the activation energy of the last stage, which would presumably be rate-determining, can be obtained by considering the general scheme of the addition of the Br_3 molecule

³⁷ Sherman and Sun, Ref. 35; *cf.*, R. M. Purkayasta and J. C. Ghosh, *J. Ind. Chem. Soc.* **2**, 261 (1926); **4**, 409, 553 (1927); W. H. Bauer and F. Daniels, *J. Am. Chem. Soc.*, **56**, 738 (1934).

to a —C=C— bond system. This may be treated as a five-electron problem, and the representation of the potential-energy surface is simplified by supposing that the linear Br_3 molecule approaches the —C=C— system in one plane, as depicted in Fig. 61. As in the case of the addition of the halogen molecule (page 244), the carbon-carbon bond distance is assumed to have the constant value of 1.46 \AA . Reaction between Br_3 and the carbon-carbon system is accompanied by a decrease in r_1 and an increase of r_2 ; hence, the potential-energy surface can be plotted in terms of these two parameters. By making

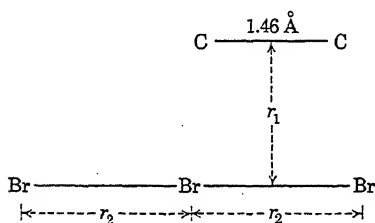
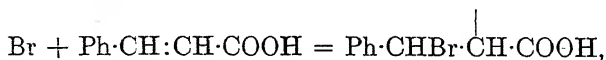


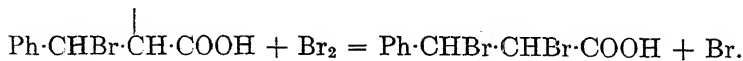
FIG. 61.—Approach of triatomic bromine molecule to a double bond.

the assumption that 14 per cent of the diatomic bonding energy is coulombic in character, the activation energy of the process under consideration is found to be 35.6 kcal. The reaction between Br_3 and ethylene will thus presumably require an activation energy of about 36 kcal., which is appreciably

greater than that given in Table XIX for the addition of Br_2 to ethylene; it is improbable, therefore, that Br_3 molecules will play an important part in the bromination of ethylene. Although it is unlikely that the results obtained here for the activation energies of the addition of Br_3 and Br_2 to a double bond will hold exactly for the bromination of cinnamic acid in solution, it is not improbable that the difference in the two activation energies will be of the same order. It appears, therefore, that the mechanism given above, involving reaction between cinnamic acid and Br_3 , is incorrect. A more probable mechanism is the following: bromine atoms are formed in the primary photochemical stage, and these react thus:

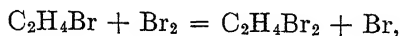


followed by



The activation energy of the first stage will undoubtedly be small, for it is of the nature of an association reaction, and that of the

second stage will be similar to the activation energy for the reaction



which is only 2.3 kcal. (see Table XX).

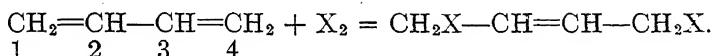
Calculations similar to those described for Br_2 have also been made for the addition of Cl_3 and I_3 to a double bond; the results are given in Table XXI, although they are of no immediate practical interest.

TABLE XXI.—ACTIVATION ENERGIES FOR ETHYLENE-TRIATOMIC HALOGEN REACTIONS

Reaction	<i>E</i> , kcal.
$\text{C}_2\text{H}_4 + \text{I}_3 = \text{C}_2\text{H}_4\text{I}_2 + \text{I}$	29.7
$\text{C}_2\text{H}_4 + \text{Br}_3 = \text{C}_2\text{H}_4\text{Br}_2 + \text{Br}$	35.6
$\text{C}_2\text{H}_4 + \text{Cl}_3 = \text{C}_2\text{H}_4\text{Cl}_2 + \text{Cl}$	48.2

In no case, therefore, in the addition of a halogen to a double bond, is the reaction involving the triatomic molecule likely to take preference over that with the diatomic molecule.

Addition of Halogens to Conjugate Double Bonds.³⁸—It is well known that the reaction of a diatomic molecule with a conjugated double-bond system frequently results in 1-4 addition, rather than addition in the 1-2 or 3-4 positions. Thus,



Various explanations of the phenomenon have been proposed by organic chemists,³⁹ but there seemed to be a possibility that the calculation of the activation energies required for 1-4 and 1-2 addition, respectively, might throw some light on the subject. The valence angle between a single and a double bond of a carbon atom is $125^\circ 16'$; but since there is the possibility of free rotation about the single bond joining the 2- and 3-carbon atoms, the exact configuration of a conjugated system of double bonds is not known. For the purpose of the present calculations, it will be supposed that the chain of carbon atoms is in the most

³⁸ H. Eyring, A. Sherman and G. E. Kimball, *J. Chem. Phys.*, **1**, 586 (1933); see also L. S. Kassel, *ibid.*, **1**, 749 (1933).

³⁹ See, for example, J. Thiele, *Ann.*, **306**, 87 (1899); E. Erlenmeyer, *ibid.*, **316**, 43 (1901); A. Lapworth, *J. Chem. Soc.*, **121**, 416 (1922); W. O. Kermack and R. Robinson, *ibid.*, **121**, 427 (1922).

favorable state for the attachment of two atoms, *e.g.*, of bromine, in the 1- and 4-positions. The four carbon atoms will then be in one plane, and the 1- and 4-atoms will lie on the same side of the line joining the 2- and 3-atoms, as indicated in Fig. 62. By assuming that the C—C distances have the fixed value of

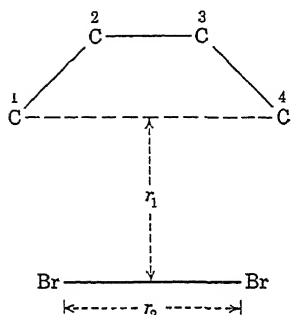


FIG. 62.—Addition of bromine molecule to 1-4 carbon atoms.

1.46 Å., the valence angle still being 125 deg., and that the bromine molecule approaches the conjugate double-bond system in the symmetrical manner depicted, the configuration can, as in the previous cases, be completely specified by two coordinates r_1 and r_2 . Initially, r_1 is large and r_2 is the normal interatomic distance in molecular bromine, taken as 2.28 Å.; in the course of the reaction, r_1 decreases while r_2 increases until the C—Br distance is that corresponding to a single bond (1.91 Å.). If,

as in other instances, the influence of the potential energy of the system of all electrons except those immediately concerned in the reaction is ignored, the problem reduces to one of the rearrangement of six electrons, as in Fig. 63. The carbon atom pairs 1-2, 2-3 and 3-4 are joined by additional pairs of electrons in each case; these are not shown, for their positions are pre-

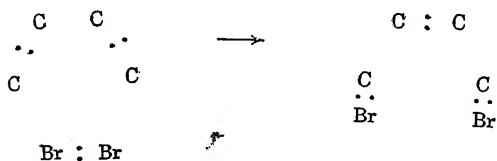


FIG. 63.—Addition of bromine molecule to 1-4 carbon atoms as a six-electron problem.

sumably unchanged by the reaction. If the directional effect of the *p*-electrons is neglected, it is possible to calculate the potential energy of the system by an extension of the method already described for four electrons in Chap. II. The potential-energy surface for the reaction involving 1-4 addition of bromine to a conjugated double-bond system, obtained in this manner, on the basis of 14 per cent of additive energy of binding, is

shown in Fig. 64; the reaction path is indicated by the arrows, and the activation energy is seen to be about 31 kcal. If the molecule of bromine does not approach in the same plane as the four carbon atoms, as postulated above, the activation energy would be higher; for example, if the direction of approach is perpendicular to this plane, the activation energy is calculated to be 65 kcal., whereas if the line of approach made an angle of 109 deg. with it the energy of activation would be 40 kcal. The activated complex in which all six atoms are in one plane

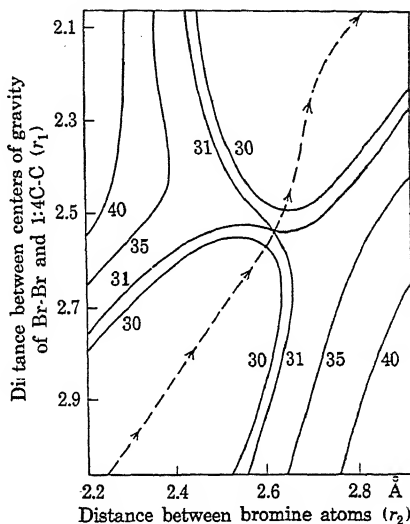


FIG. 64.—Potential-energy surface for addition of bromine molecule to 1-4 carbon atoms. (Eyring, Sherman and Kimball.)

thus has the minimum potential energy, and this may be regarded as giving the path by which the majority of bromine, or other diatomic molecules, will react with a conjugated system of double bonds.

The 1-4 addition of hydrogen has been treated in the same manner, and the energy of activation has been calculated to be 64 kcal.

The activation energy for 1-2 addition has been derived by a similar procedure, on the assumption that the adding molecule approaches in the plane of the four carbon atoms in the manner shown in Fig. 65. The potential energy is again reduced to a function of two parameters only, and the activation energy for

the addition of bromine is found to be 42 kcal. and for hydrogen about 82 kcal. In this case, also, if the molecule being added approached in any other direction, the potential energy of the activated state would be greater.

Comparing the calculated activation energies for 1-4 and 1-2 addition, it is evident that the former reaction would be expected to occur more readily than the latter. It should be noted, however, that the energies of activation for the addition of bromine are of the order of 30 to 40 kcal., so that the *homogeneous* reaction would take place very slowly at ordinary temperatures. Actually the addition

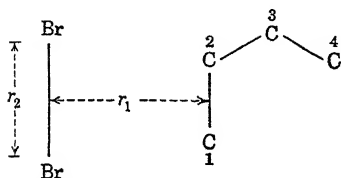
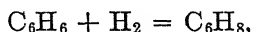


FIG. 65.—Addition of bromine molecule to 1-2 carbon atoms.

is relatively rapid, so that the process must involve a catalytic mechanism; this is in agreement with experiment, for it has been found that the reaction between gaseous bromine and butadiene takes place largely on the surface

of the reaction vessel.⁴⁰ A detailed consideration of the potential energies for possible surface reactions is too complicated to be carried out at present, and unfortunately the approximate treatments that have hitherto been attempted do not lead to conclusive results.

Addition to Benzene.⁴¹—In the reaction between hydrogen and benzene, *viz.*,



it is necessary to consider eight electrons, one on each atom of the hydrogen molecule and six, which do not form unique bonds, on the carbon atoms of the benzene ring. The secular equation for the eight-electron problem is of the fourteenth order, but in the present instance this can be simplified, as a result of symmetry, to the product of fourth- and tenth-degree equations; the latter only has to be solved in order to give the potential energy of the activated state. The molecule of hydrogen is assumed to approach the benzene molecule in a direction making

⁴⁰ G. B. Heisig, *J. Am. Chem. Soc.*, **55**, 1297 (1933); see also A. Sherman and H. Eyring, *ibid.*, **54**, 2661 (1932).

⁴¹ A. Sherman, C. E. Sun and H. Eyring, *J. Chem. Phys.*, **3**, 49 (1935).

such an angle with the plane of the ring as corresponds to that made by the new C—H bonds in the product, 1:2-dihydrobenzene. The carbon-carbon distances are supposed to remain constant throughout the reaction, in which r_1 decreases as r_2 increases. The various integrals required for the solution of the problem are evaluated from the Morse potential-energy equations, the assumption being made that the value of these integrals is a function only of the distance between the two atoms concerned. On the basis of 14 per cent of additive energy, the potential-energy surface indicates an activation energy of about 95 kcal. It is improbable, however, that this result is correct, for the calculations suggest that the final state, *i.e.*, 1:2-dihydrobenzene, is 85 kcal. less stable than benzene, *i.e.*, ΔH for $C_6H_6 + H_2$ is +85 kcal., whereas the thermochemical data indicate that the dihydro-compound is slightly more stable.

Satisfactory resonance energies, which are believed to represent the difference between the observed heats of formation and those calculated from bond strengths, may be obtained by assuming that the exchange integrals between all pairs of electrons other than those on neighboring atoms are zero; it seems possible, therefore, that similar agreement might be obtained by employing the same approximation in the case under examination. If the exchange integrals between electrons on nonbonded pairs of atoms are neglected, *i.e.*, if the exchange integrals $ab, bc, cd, de, ef, fa, eg, fh$ and gh (Fig. 66) are the only ones included, ΔH is calculated to be 26 kcal., which is much closer to the experimental value. By increasing the C—H bond energy to a small extent, the agreement can be improved still further. Although the approximation that interactions between neighboring atoms only need be considered for initial and final states gives a reasonably satisfactory result for ΔH , it cannot be applicable to the whole potential-energy surface, for it would lead to an activation energy of 36 kcal. This value is clearly too low, for it is less than is required for the hydrogenation of ethylene, *i.e.*, 43 kcal., and the latter process is known to take

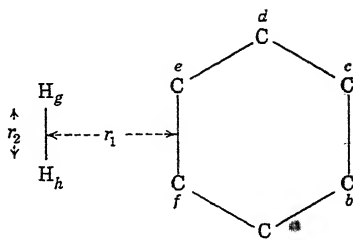


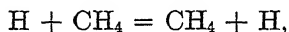
FIG. 66.—Addition of a hydrogen molecule to benzene.

place more rapidly than that between hydrogen and benzene. Further, an activation energy of 36 kcal. would mean an appreciable homogeneous reaction rate at temperatures below 500°K., whereas, in actual fact, it is necessary to use a catalyst to hydrogenate benzene in the temperature range of 500 to 550°K.⁴²

Another possibility, which seems very reasonable, is to set the exchange integrals for all nonadjacent atoms,⁴³ except *eh* and *fg*, equal to zero; this gives an activation energy of about 80 kcal. with a relatively small value for ΔH . It might be imagined that equally good agreement could be obtained by neglecting the electrons *a*, *b*, *c* and *d* altogether, so that the system was reduced to one of four electrons; the reaction would now be essentially the same as that between ethylene and hydrogen, but as already noted, the latter process is more rapid than the hydrogenation of benzene and involves a different ΔH value. It seems, therefore, that results in best agreement with experiment are obtained by taking into account only the exchange integrals *eh* and *fg*, which it is evident cannot be neglected, in addition to those for electrons on neighboring atoms.

HYDROCARBON REACTIONS

Hydrogen Exchange Reaction.⁴⁴—The exchange type of reaction,



in which the approaching hydrogen atom becomes attached to the carbon and in doing so drives off one of the hydrogen atoms of the original methane molecule, is one which may be represented diagrammatically by Fig. 67, where r_1 is the distance from the approaching hydrogen to the carbon atom and r_2 is that between the carbon and the hydrogen atom which is eventually expelled. The valence angle between the C—H bond that is broken and any of the other C—H bonds is θ ; symmetry considerations show that this must be the same for all three possible cases. At the beginning of the reaction, r_1 is large and r_2 has the normal

⁴² See, for example, G. Dougherty and H. S. Taylor, *J. Phys. Chem.*, **27**, 533 (1923); P. Sabatier, *Ind. Eng. Chem.*, **18**, 1006 (1926).

⁴³ Cf. L. Pauling, *J. Chem. Phys.*, **1**, 362, 606 (1933).

⁴⁴ E. Gorin, W. Kauzmann, J. Walter and H. Eyring, *ibid.*, **7**, 633 (1939).

value for a C—H bond; at the completion of the process, the positions are reversed, for r_2 is now large and r_1 is equal to the normal C—H distance. The system may be regarded as a three-electron problem, one electron being on each of the two hydrogen atoms immediately concerned in the exchange and one on the carbon atom. The potential-energy surface has been calculated as a function of r_1 , r_2 and θ , it being assumed that 10 per cent of the energy of the H—H bond is additive but that the exchange energy of the C—H bond varies with the angle θ ; the values, in the latter case, are obtained with the aid of the integrals proposed by J. H. Van Vleck.⁴⁵ For any given angle, however, the coulombic energy is assumed to vary with the C—H distance in the same way as does the total binding energy, given by the Morse curve, for this bond. The activation energy for the reaction is found to be 37 kcal., and the activated state has a symmetrical configuration, as may be expected, with

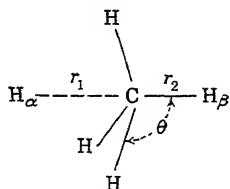


FIG. 67.—Exchange reaction between a hydrogen atom and methane.

$$r_1 = r_2 = 1.30 \text{ \AA.}$$

and $\theta = 90$ deg. It appears, therefore, that as the hydrogen atom H_α approaches the methane molecule, the distant atom H_β is repelled while at the same time the other three hydrogen atoms are forced into a plane, as indicated in Fig. 68. The activated state occurs when H_α and H_β are equidistant from the carbon atom and the three other hydrogen atoms are in the same plane as the carbon.

Inversion Reactions.⁴⁶—The calculation made in connection with the inversion of methane may be applied to the racemization of optically active alkyl iodides, *e.g.*, $RR'R''CI$, by means of iodine atoms in the gas phase. The mechanism of the process is that the iodine atom approaches the alkyl iodide just as the hydrogen atom does in the methane molecule in Fig. 68, and a

⁴⁵ J. H. Van Vleck, *ibid.*, **1**, 183 (1933); see also H. H. Voge, *ibid.*, **4**, 581 (1936).

⁴⁶ Gorin *et al.*, Ref. 44; E. Bergmann, M. Polanyi and A. Szábo, *Z. physik. Chem.*, **B**, **20**, 161 (1933); R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, **31**, 482 (1935); *cf.* F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).

symmetrical activated complex is formed with the R, R' and R'' radicals in a plane passing through the central carbon atom and an iodine atom symmetrically disposed on each side. There is an equal probability that each of these two atoms will be expelled from the complex; half the activated complexes will thus revert to the original state, and the other half will have an inverted configuration. If the initial molecule $RR'R''CI$ was optically active, the product will thus be racemic, for the inversion reaction can take place equally with either *d*- or *l*-forms. The energy of activation of the inversion process will depend on the strength of the bond formed between the approaching iodine atom and the central carbon atom, as may be seen from the following considerations. The activated state may be regarded as a planar CR_3 or CH_3 radical with an iodine atom, or other atom,

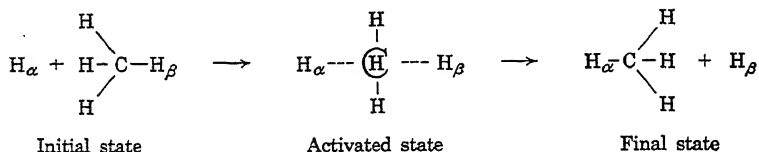
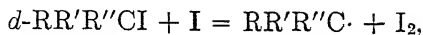


FIG. 68.—Mechanism of inversion type of exchange reaction between a hydrogen atom and methane.

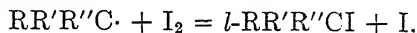
on each side; since the planar configuration is the stable one for the free radical, the potential energy will be mainly dependent on the atoms concerned in the exchange. One of these has to be brought closer to the central carbon atom and the other pushed farther away, and the amount of energy required to accomplish this process is clearly dependent on the strength of the C—I bond, or of the C—H bond in the case of methane. It may be supposed, as a rough approximation, that the energy of activation for the inversion reaction is directly proportional to this bond strength; since the energy required for the inversion of the methane is about 37 kcal., that for the optical inversion of the compound $RR'R''CI$, brought about by iodine atoms, should be approximately $37 \times \frac{40}{100}$, *i.e.*, 15 kcal., the strength of the C—H and C—I bonds being taken as 100 and 40 kcal., respectively. The experimental values are of the order of 14 to 18 kcal., which are in good agreement with the calculated figure.

It may be noted that in addition to the inversion mechanism proposed above, an alternative one, involving the actual forma-

tion of a free radical, thus,



followed by



is possible. The first stage is probably rate-determining, and the activation energy may be estimated in the following manner. Since the reaction involves the breaking of a C—I bond, requiring 40 kcal., and the making of an I—I bond, giving up 34 kcal., the process is endothermic to the extent of 6 kcal. Apart from this, the normal activation energy for a reaction between a molecule and an atom, *e.g.*, $\text{H}_2 + \text{H}$ or $\text{H}_2 + \text{Cl}$, is about 8 kcal.; and so the energy of activation of the reaction between $d\text{-RR'R''CI}$ and iodine atoms should be about 14 kcal. The free radical mechanism is thus a possibility in this particular instance.

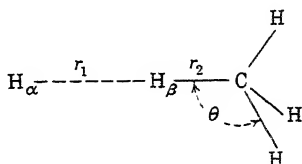
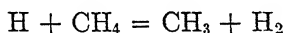


FIG. 69.—Model for reaction between atomic hydrogen and methane.

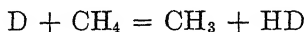
Hydrocarbon-Hydrogen Reactions.⁴⁷—The potential-energy surface for the reaction



has been considered (page 135) in connection with the possible existence of the stable complex CH_5 , and further reference to the subject will be made below. In the meantime the activation energy for the complex reaction will be considered. The configuration of the reactants is assumed to be as in Fig. 69, and the problem may be treated as one of three electrons, one electron being on the carbon atom and one on each of the two hydrogen atoms, shown to the left of the carbon (H_α and H_β). By minimizing the energy with respect to the valence angle θ for each value of r_1 and r_2 , it is possible to draw a potential-energy surface in terms of these two coordinates only. The activated complex has the dimensions $r_1 = 1.40 \text{ \AA.}$, $r_2 = 1.17 \text{ \AA.}$ and $\theta = 105 \text{ deg.}$; and the energy, on the basis of the same assumptions as on page 255 concerning the proportion of coulombic energy, is

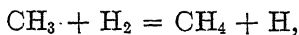
⁴⁷ Gorin *et al.*, Ref. 44.

9.5 kcal. greater than the initial state. The activation energy for the reaction



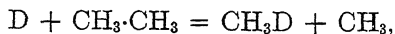
may be expected to be about 1 kcal. greater because of the difference in the zero-point energies of C—D and C—H bonds in the activated state. From the investigation of various processes apparently involving the reaction under discussion as the rate-determining stage, the activation energy is found to be 13 ± 2 kcal., which is in good agreement with the calculated value.

The reverse of the reaction under consideration, *i.e.*,

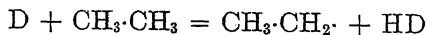


has been studied by a number of workers, and the energy of activation found to be 11 ± 2 kcal.⁴⁸ This means that the heat of reaction must be between zero and 6 kcal.; the theoretical value estimated from the potential energy surface is 7.4 kcal.

The reaction between deuterium atoms and ethane at ordinary temperatures is accompanied by the formation of extensive amounts of deuteromethanes,⁴⁹ and it has been suggested that the initial stage of the process is



which is analogous to the inversion type of reaction considered above for methane. In the present case the deuterium atom approaches one methyl group of the ethane, and as a result the other is eventually expelled; since the strength of the C—C bond is little less than that of C—H, the activation energy of this reaction should be at least 30 kcal. The experimental value is 7.2 kcal., and so it seems that an alternative mechanism should be sought. One possibility⁵⁰ is based on the reaction



⁴⁸ H. von Hartel and M. Polanyi, *Z. physik. Chem.*, **B**, 11, 97 (1930); H. S. Taylor and C. Rosenblum, *J. Chem. Phys.*, **6**, 119 (1938).

⁴⁹ N. R. Trenner, K. Morikawa and H. S. Taylor, *ibid.*, **5**, 203 (1937); E. W. R. Steacie, *ibid.*, **6**, 38 (1938).

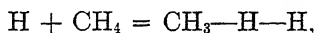
⁵⁰ H. S. Taylor, *J. Phys. Chem.*, **42**, 763 (1938).

as the first stage; this process is similar to

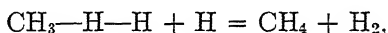


for which the activation energy, as calculated above, is 95. kcal. The subsequent stages, in which atoms and radicals are involved, probably require only small activation energies.

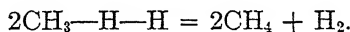
The suggested relative stability of the $\text{CH}_3\text{—H—H}$ complex (page 135) can be used to account for some interesting phenomena observed in connection with the ortho-para hydrogen conversion and the hydrogen-deuterium exchange reaction in the presence of water vapor, ammonia or methane.⁵¹ Water or ammonia causes little decrease in the rate of conversion of ortho- to para-hydrogen induced by excited mercury atoms at ordinary temperatures, but above 150°C. the rate is slowed down markedly by methane. This suggests that methane removes hydrogen atoms from the system to a very appreciable extent; thus, at 238°C. it appears that methane reduces the concentration of hydrogen atoms to one-eighth the value in the absence of the hydrocarbon. It is possible, therefore, that the methane acts as a catalyst for the recombination of hydrogen atoms by the reaction



followed by



or by



Before the complex $\text{CH}_3\text{—H—H}$ can be formed, the system must pass over an energy barrier of about 10 kcal. in height (see Fig. 40, page 135), and this would account for the influence of the methane becoming noticeable at 150°C. and increasing as the temperature is raised. At 280°C., however, the effect reaches a maximum and decreases beyond this temperature. Such a result is not unexpected since the bond between methane and the hydrogen atom is relatively weak, and hence the equilibrium will be in favor of the dissociated form at moderately high temperatures.

It is of interest to mention that the low hydrogen-atom concentration in the photochemical decomposition of ammonia has

⁵¹ A. Farkas and H. W. Melville, *Proc. Roy. Soc.*, **157**, A, 625 (1936).

been attributed to the formation of an NH_4 radical.⁵² It is established that if this is formed the four hydrogen atoms cannot be equivalent, since no exchange reaction occurs in the presence of deuterium atoms.⁵³ It appears possible, therefore, that a complex $\text{NH}_2\text{—H—H}$ is formed, analogous to $\text{CH}_3\text{—H—H}$. In view of the similarity in strengths of the C—H and N—H bonds and of the interatomic distances, it is possible that the calculation which led to the conclusion that $\text{CH}_3\text{—H—H}$ is stable would lead to an analogous conclusion concerning the $\text{NH}_2\text{—H—H}$ complex.

Combination of Free Radicals and the Dissociation of Ethane.⁵⁴

The rate of combination of methyl radicals to form ethane can be calculated by means of the theory of absolute reaction rates in a manner exactly analogous to that employed in connection with the reaction between a hydrogen molecule and molecule ion (page 220). As explained in Chap. III (page 131), the apparent activation energy $E_{\text{act.}}$ in the reaction between two free radicals arises because of the action of opposing rotational and polarization energies, and the result is

$$E_{\text{act.}} = \frac{[J(J+1)\hbar^2]}{72(\pi^2\mu)^{3/2}[\alpha_A\alpha_B(\mathcal{G}_A\mathcal{G}_B/\mathcal{G}_A + \mathcal{G}_B)]^{1/2}} \quad (33)$$

where α_A and α_B and \mathcal{G}_A and \mathcal{G}_B are the polarizabilities and ionization potentials of the free radicals A and B, respectively, μ is the reduced mass of the activated complex and J is the rotational quantum number. For the reasons given previously (page 121), the rotational and vibrational partition functions in the rate equation cancel, and hence

$$k = \frac{\frac{(2\pi m_{\ddagger} kT)^{3/2}}{\hbar^3}}{\frac{(2\pi m_A kT)^{3/2}}{\hbar^3} \cdot \frac{(2\pi m_B kT)^{3/2}}{\hbar^3}} \times \frac{\left[1 + \sum_{J=1}^{\infty} (2J+1) e^{-E/kT}\right]}{\sigma_{\ddagger}} \cdot \frac{kT}{\hbar}, \quad (34)$$

⁵² A. Farkas and P. Hartek, *Z. physik. Chem.*, **B**, 25, 257 (1937).

⁵³ H. S. Taylor and J. C. Jungers, *J. Chem. Phys.*, **2**, 452 (1934).

⁵⁴ E. Gorin, *Acta Physicochim. U.R.S.S.*, **9**, 691 (1938); Gorin *et al.*, Ref. 44.

where m_A , m_B and $m_‡$ are the masses of A and B and of the activated complex, respectively, and $\sigma_‡$ is the symmetry number of the latter. Upon replacing the summation in the square brackets by integration, as on page 222, it is found that

$$k = \kappa 2^{3/2} 3^{1/2} \Gamma\left(\frac{3}{2}\right) \frac{\pi^{1/2} (kT)^{1/2}}{\sigma_‡} \left[\alpha_A \alpha_B \left(\frac{g_A g_B}{g_A + g_B} \right) \right]^{1/2} \left(\frac{m_A + m_B}{m_A m_B} \right)^{1/2} \quad (35)$$

where $\Gamma(\frac{3}{2})$ is the gamma function of $\frac{3}{2}$.

For the combination of two methyl radicals to form ethane, $\sigma_‡$ is 2, and the polarizability of the free methyl radical may be taken as 2.5×10^{-24} which is slightly greater than the value for the bound radical, *i.e.*, 2.25×10^{-24} cc. The ionization potential of the radical has been calculated as 8.4 volts,⁵⁵ and insertion of these data in the correct units in Eq. (35) gives for the specific rate of the combination of two methyl radicals at 873°K. a value of about

$$k = 2 \times 10^{-11} \text{ cc. molecule}^{-1} \text{ sec.}^{-1},$$

on the assumption that the transmission coefficient is unity. It should be pointed out that this figure is a maximum because it has been assumed that the radicals rotate freely in the activated state. If this rotation is restricted, so as to be of the nature of a weak vibration, or a libration, the specific reaction rate would be lowered by a factor of 2 or 3. Further, at moderately low pressures an appreciable proportion of the activated complexes may redissociate before they are stabilized by collisions with another molecule; the transmission coefficient would thus be less than unity and so would serve to decrease the rate to some extent.

The result derived above may be utilized to calculate the rate of dissociation of ethane into two methyl radicals; for this purpose, it is necessary to determine the equilibrium constant of the reaction K , for $k_f = k_b K$, where k_f is the specific rate of the forward reaction, *i.e.*, dissociation of ethane, and k_b is that of

* The numerical factors in the equations given in references (44) and (54) differ somewhat from those in Eq. (35); the discrepancy, however, is not large.

⁵⁵ R. S. Mulliken, *J. Chem. Phys.*, **1**, 492 (1933).

the reverse reaction as determined above. It follows, therefore, that

$$K = \frac{k_f}{k_b} = \frac{F_{\text{CH}_3^2}}{F_{\text{C}_2\text{H}_6}} e^{-\Delta E_0/RT}, \quad (36)$$

where ΔE_0 is the heat of reaction, at constant volume, at the absolute zero, and F_{CH_3} and $F_{\text{C}_2\text{H}_6}$ are the partition functions for unit volume of methyl radicals and ethane, respectively. The term F_{CH_3} is defined by

$$F_{\text{CH}_3} = F_{\text{tr}} F_{\text{vib}} F_{\text{rot}} \quad (37)$$

in the usual manner; but in $F_{\text{C}_2\text{H}_6}$ it is necessary to include the contribution of internal rotation, thus:

$$F_{\text{C}_2\text{H}_6} = F_{\text{tr}} F_{\text{vib}} F_{\text{rot}} F_{\text{int. rot.}} \quad (38)$$

The vibration frequencies of the methyl group were taken from those in methyl iodide,⁵⁶ viz., 1,252, 2,860, 1,445 and 3,074 cm^{-1} , the last two being doubly degenerate; and from these F_{vib} was calculated in the usual manner. The rotational partition function of the methyl group was obtained from the equation

$$F_{\text{rot}} = \frac{8\pi^2(8\pi^3 I_z^2 I_z)^{1/2}}{\sigma h^3}, \quad (39)$$

the moments of inertia, assuming a planar configuration, viz., $I_z = \frac{1}{2}I_x = 6.3 \times 10^{-40}$ g. cm^2 , being derived from the known normal C—H distance. The symmetry number σ for the methyl group is 6, since the molecule is flat, and the plane of the molecule is a plane of symmetry.

To evaluate F_{vib} for ethane, the frequencies⁵⁷ employed were 993, 1,460, 2,927, 1,380, 2,960, cm^{-1} , and the doubly degenerate frequencies 827, 1,480, 3,000, 1,005, 1,575 and 3,025 cm^{-1} . Equation (39) was used for the rotational partition function, the moments of inertia being $I_z = 40.1$ and $I_x = 10.8 \times 10^{-40}$ g. cm^2 ; the symmetry number for ethane is 18.⁵⁸ The partition function for internal rotation is computed by regarding energy levels of height less than that of the energy barrier preventing free rota-

⁵⁶ H. Sponer, "Molekülspektren," Vol. I, p. 85, Verlag J. Springer, Berlin, 1935.

⁵⁷ J. B. Howard, *J. Chem. Phys.*, **5**, 442 (1937).

⁵⁸ J. D. Kemp and K. S. Pitzer, *J. Am. Chem. Soc.*, **59**, 276 (1937).

tion as being equivalent to a harmonic oscillation (libration) whose force constant is obtained from the potential function for this barrier in the vicinity of the minimum. The function is of the form

$$V = \frac{1}{2}V_0(1 - \cos 3\theta) \quad (40)$$

where V is the potential energy corresponding to the angle of rotation θ ; the maximum height of the barrier (V_0) is 3,000 cal. The lowest frequency is then found to be 306 cm.^{-1} , which is equivalent to 887 cal. per mole. The height of the barrier preventing rotation is about 2,560 cal. above the lowest level, allowing for zero-point energy, and so the contribution to $F_{\text{int. rot.}}$ of the levels below the top of the barrier preventing rotation is given by

$$3(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + e^{-2,560/RT}). \quad (41)$$

It will be noted that the third term is not $e^{-3h\nu/kT}$, since the energy would be equivalent to 3×887 , *i.e.*, 2,661 cal. per mole, which would bring the level above the top of the barrier. The factor 3 in front of the expression arises because there are three equilibrium positions, resulting from rotation of one methyl group with respect to the other, about which the restricted rotation can occur. To this quantity must be added the contribution for the internal rotational levels of energy exceeding 2,560 cal. per mole. If the partition function for a one-dimensional rotator is used, this becomes

$$e^{-2,560/RT} (8\pi^2 I kT)^{1/2} \quad (42)$$

where I is equal to $\frac{1}{2}I_x$, *i.e.*, $5.4 \times 10^{-40} \text{ g. cm.}^2$

Insertion of the partition functions derived in this manner into Eq. (36) gives, for the equilibrium constant between ethane and methyl radicals,

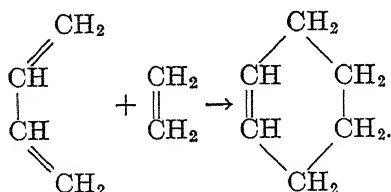
$$K = 2.5 \times 10^{25} \times e^{-\Delta E_0/RT},$$

with concentrations in molecules per cubic centimeter. If the value of k_b for the combination of methyl radicals, given above, is used, it is seen that the specific rate constant k_f for the dissociation of ethane is

$$k_f = 5 \times 10^{14} \times e^{-\Delta E_0/RT} \text{ sec.}^{-1}$$

This value may be reduced by a factor of 2 or 3 by taking into account the restriction of free rotation in the activated complex, as mentioned previously.

Diene-addition Reactions.⁵⁹—The simplest type of reaction, for theoretical consideration, of the addition of an unsaturated compound to a hydrocarbon with a pair of conjugate double bonds (Diels-Alder reaction) is the addition of ethylene to butadiene, thus:



If the electronic structures of the reactants and resultants are considered, it is seen that the process involves the rearrangement of six mobile electrons, and these only need to be considered in order to evaluate the potential energy of the system. The Rumer set of five independent bond eigenfunctions (*cf.* page 60), ψ_1 , ψ_2 , ψ_3 , ψ_4 and ψ_5 , can then be represented as in Fig. 70. The

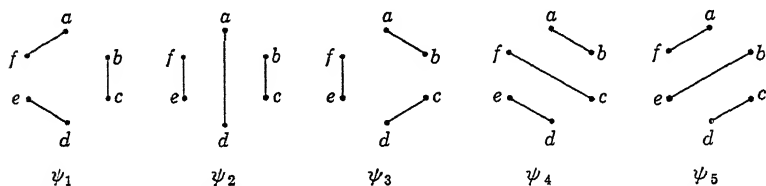


FIG. 70.—Representation of five independent bond eigenfunctions for addition of ethylene to butadiene.

initial state can be defined in terms of ψ_1 and ψ_2 , and the final state is given by ψ_3 ; all five representations are required to define the activated state. If the ethylene molecule is supposed to approach the butadiene molecule in a symmetrical manner as depicted in Fig. 71, the fifth-order secular equation reduces to one of the fourth order; further simplification can be made by neglecting exchange integrals between nonadjacent carbon atoms. The exchange integrals af , fe , ed and bc are derived from the

⁵⁹ M. G. Evans and E. Warhurst, *Trans. Faraday Soc.*, **34**, 614 (1938); M. G. Evans, *ibid.*, **35**, 824 (1939).

Morse curves for the difference between C—C and C=C bonds, on the assumption of a definite proportion of coulombic energy, and the integrals ab and cd are obtained from the C—C potential-energy curve. As a first approximation, it is assumed that the distances af , fe , ed and bc in the initial state are all equal to the normal distance between double-bonded carbon atoms, and a correction is then applied for the compression of the single bond fe from its normal value in butadiene, *viz.*, 1.41 Å., to the double-bond distance.

If the coulombic energy is taken as 10 per cent of the total binding energy, the energy of activation of the reaction is found to be 17 kcal., whereas for 15 per cent coulombic energy the result is 15 kcal. These values are in good agreement with those obtained experimentally⁶⁰ for a number of Diels-Alder reactions, as may be seen from the data in Table XXII.

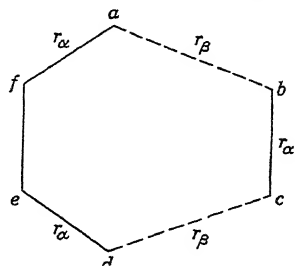


FIG. 71.—Symmetrical approach of ethylene to butadiene; r_α is the normal double-bond distance.

TABLE XXII.—EXPERIMENTAL ACTIVATION ENERGIES FOR DIELS-ALDER REACTIONS

Reaction	Activation Energy, kcal.
Acrolein + isoprene.....	18.7
Acrolein + butadiene.....	19.7
Acrolein + cyclopentadiene.....	15.2
Crotonic aldehyde + butadiene.....	22.0

The calculated activation energy does not take into account the influence of the group, *e.g.*, —CHO, substituted in the ethylene molecule; this would, of course, have some influence on the results, but the effect is evidently small.

The possibility has been examined⁶¹ of calculating the activation energy for diene-addition reactions by determining the lowest point at which the surface, for the variation of the potential energy E_2 of the final state with the distances of the bonds ab and cd , cuts the repulsion-energy E_1 surface, for the symmetri-

⁶⁰ G. B. Kistiakowsky and J. R. Lacher, *J. Am. Chem. Soc.*, **58**, 123 (1936).

⁶¹ Evans, Ref. 59.

cal approach of *bc* to *afed* (cf. page 142). This would give the correct activation energy if the resonance energy in the activated state were negligibly small. The E_2 curve is determined from the potential energy required to extend the two C—C bonds *ab* and *cd*; the other distances may be regarded as merely changing the zero to which the potential energy is referred. The necessary zero correction can be estimated from the Morse equations for C—C and C=C by considering the changes in length of the bonds *de*, *ef*, *af* and *bc* from final to initial states. The repulsion curve E_1 may be calculated by the approximate relationship (cf. page 144)

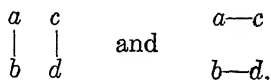
$$E_1 = Q_{ab} + Q_{cd} - \frac{1}{2}(\alpha_{ab} + \alpha_{cd}), \quad (43)$$

where the Q terms refer to the coulombic energies and the α 's to the exchange contributions; in this expression the interactions between all nonadjacent carbon centers have been neglected. Since $Q + \alpha$ represents the C—C bond energy, it is possible, if the usual assumption concerning the relative amounts of the two forms of binding energy is made, to derive Q and α separately, for various distances of separation, by means of the Morse equation. Working in this manner the lowest crossing point of the E_1 and E_2 curves is found to correspond to an activation energy of 37 kcal. for 15 per cent coulombic energy and 32 kcal. for 10 per cent of this form of binding energy. These values are much higher than those recorded in Table XXII, and so it is evident that in reactions of the type under consideration it is not permissible to neglect the resonance energy in the activated state. Such a conclusion is not surprising when it is realized that the complete description of this state requires resonance between five canonical structures, as shown above.

It is of interest to mention that the dimerization reactions of ethylene, propylene, butylene and amylene all require activation energies of about 38 kcal.,⁶² this is very close to the calculated value recorded above for the addition of ethylene to butadiene, resonance energy being neglected. It appears probable, therefore, that in these dimerization processes there is little resonance

⁶² H. M. Stanley, J. E. Youell and J. B. Dymock, *J. Soc. Chem. Ind.*, **53**, 206 (1934); M. V. Krauze, M. S. Nemtsov and E. A. Soskina, *Compt. rend. U.R.S.S.*, **3**, 262, 301 (1934); *J. Gen. Chem. U.S.S.R.*, **5**, 343, 382 (1935).

energy in the activated state; this is not unexpected since two bond eigenfunctions only, represented by



are sufficient to describe fully the initial, final and activated states. When the olefin molecules concerned in the reaction possess a pair of conjugated double bonds, however, there is resonance among several structures in the activated state. According to quantum-mechanical calculations the resonance energy in a radical of the type that might well represent the activated complex is about 15 kcal. An activation energy of $38 - 15$, *i.e.*, 23 kcal., would thus appear to be reasonable. The experimental values for the dimerization of butadiene, methyl butadiene and pentadiene are all of the order of 25 kcal.

Dimerization of Ethylene.—It was shown on page 195 that the question of the frequency factor could be approached from the standpoint of entropy, and this aspect of the subject is well illustrated by the dimerization of ethylene.⁶³ It has been known for some time that the observed rate of polymerization of ethylene to butylene is about 2,000 times slower than the value calculated from the simple collision theory, using the experimental activation energy of 35.0 kcal. This discrepancy is immediately removed by the application of the absolute reaction rate theory, in the form of Eq. (158), Chap. IV; thus,

$$k_p = \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S_p^\ddagger/R}, \quad (44)$$

the transmission coefficient being assumed to be unity. The primary product of the bimolecular association of ethylene is undoubtedly a butylene, and it is probable that its structure is similar to that of butene-1; the reasonable assumption may therefore be made that if the activated complex is linear it will have the same entropy as this particular butylene. The difference of entropy between a mole of butene-1 and two moles of ethylene is -30.1 cal./deg. (see Table II, page 23), the standard states being the ideal gases at 1 atm. pressure and 25°C. in each case. This gives ΔS_p^\ddagger under these conditions; but to evaluate

⁶³ F. P. Jahn, *J. Am. Chem. Soc.*, **61**, 798 (1939).

the entropy change at other temperatures it is necessary to know the change in heat capacity accompanying the formation of the activated complex. The value required is the difference in heat capacity between one mole of activated complex and two moles of ethylene, and this can be estimated very approximately; as will be seen shortly, any error introduced in this manner cannot be serious. Although the activated complex has more vibrational modes than the two ethylene molecules, it is probable that the frequencies are small, so that the vibrational contributions to the heat capacities are much the same in initial and activated states. The difference in the heat capacities lies, therefore, primarily in the three translational and three rotational degrees of freedom which disappear when two molecules of ethylene are converted into the activated complex. Taking the contribution of each degree of freedom as equal to the classical value of $\frac{1}{2}R$, it follows that ΔC_p^\ddagger is about $-3R$ cal. The entropy of activation, at constant volume, at any temperature T may then be evaluated from the expression

$$\Delta S_p^\ddagger = -30.1 - 3R \ln \frac{T}{298}, \quad (45)$$

the result obtained above being utilized so that ΔS_p^\ddagger is -30.1 at 298°K .

The variation of the heat of activation ΔH^\ddagger with temperature, on the assumption that ΔC_p^\ddagger remains constant at $-3R$, is expressed by the Kirchhoff equation, thus:

$$\Delta H^\ddagger = \Delta H_0^\ddagger + T\Delta C_p^\ddagger \quad (46)$$

$$= \Delta H_0^\ddagger - 3RT. \quad (46a)$$

Inserting Eqs. (45) and (46a) in (44), taking logarithms and differentiating produce

$$\frac{d \ln k}{dT} = \frac{-2RT + \Delta H_0^\ddagger}{RT^2} \quad (47)$$

$$\therefore \frac{d \ln (kT^2)}{d(1/T)} = \frac{\Delta H_0^\ddagger}{R}, \quad (48)$$

so that ΔH_0^\ddagger can be obtained by plotting the experimental values of $\ln kT^2$ against $1/T$; in this way ΔH_0^\ddagger is found to be 36.74 kcal., and so ΔH^\ddagger at any temperature may be calculated from Eq. (46). All the information is now available to permit the calculation of

the specific reaction rates at various temperatures; the results obtained are recorded in Table XXIII.

Since the standard state for entropy has been taken as 1 atm. pressure, the rate constants given by Eq. (44) are in terms of $\text{atm.}^{-1} \text{ sec.}^{-1}$ units; for the purpose of comparison with the experimental data,⁶⁴ which are quoted in the last column in $\text{atm.}^{-1} \text{ hr.}^{-1}$ units, it is necessary to multiply by 3,600. Further, since Eq. (44) gives the rate of formation of butylene, it is necessary to introduce a factor 2, for the rate is required in terms of the disappearance of ethylene.

TABLE XXIII.—DIMERIZATION OF ETHYLENE

$T, ^\circ\text{K.}$	$-\Delta S_p^\ddagger, \text{ E.U.}$	$\Delta H^\ddagger, \text{ kcal.}$	$k, \text{ atm.}^{-1} \text{ hr.}^{-1}$	
			Calc.	Obs.
623	34.50	33.03	0.0070	0.0056
673	35.00	32.73	0.0545	0.0374
723	35.38	32.43	0.316	0.243
773	35.78	32.13	1.45	1.3

The agreement between calculated and observed velocity constants is very striking. It may be mentioned that if the values of ΔS_p^\ddagger and ΔH^\ddagger that hold at 723°K. , viz., 35.38 E.U. (calories per degree) and 32.43 kcal., respectively, are assumed to apply over the whole range of temperatures, the general agreement between experimental and calculated specific reaction rates is still good.*

Polymerization of Butadiene.⁶⁵—The experimental rate constant for the dimerization of butadiene over the range of temperature from 440 to 660°K. may be expressed by the equation

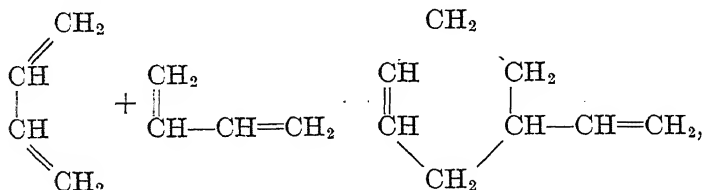
$$k = 9.2 \times 10^9 \times e^{-23,690/RT} \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

⁶⁴ R. N. Pease, *ibid.*, **53**, 613 (1931).

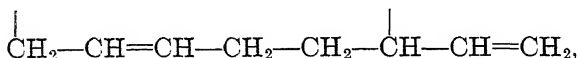
* According to Burnham and Pease (*J. Am. Chem. Soc.*, **62**, 453, 1940) the polymerization of ethylene is inhibited by nitric oxide, and the process consequently involves a chain mechanism; the observed reaction rate may thus be two or three times too high, and the agreement with the calculated rates may not be so good as appears from Table XXIII. It is nevertheless much better than is obtained from the simple collision theory.

⁶⁵ W. E. Vaughan, *ibid.*, **56**, 3863 (1932); Kistiakowsky and Lacher, *Ref. 60*; J. B. Harkness, G. B. Kistiakowsky and W. H. Mears, *J. Chem. Phys.*, **5**, 682 (1937).

The frequency factor is thus 9.2×10^9 compared with a value of about 10^{14} derived from the simple collision hypothesis. It was stated briefly in Chap. I that the discrepancy does not arise in connection with the theory of absolute reaction rates, and this subject will now be treated in some detail. The association of two molecules of butadiene results in the formation of a ring compound, 3-vinyl cyclohexene, thus,



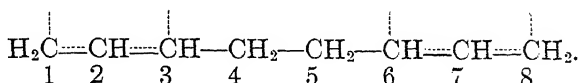
and the question arises as to whether the activated complex has a structure which is similar to that of the product, *i.e.*, in the form of a closed ring, or whether it is a free di-radical, *viz.*,



ring closure taking place subsequently by the union of the two free valences. Preliminary calculations indicated that in order to account for the experimental results by the theory of absolute reaction rates, on the assumption that the activated complex has a ring structure, vibration frequencies must be postulated which are too low for a molecule of this type. It is necessary, therefore, to consider the activated complex as a di-radical; and thus it is required, in the first place, to see if such a structure is possible energetically. It can be readily seen that the formation of the di-radical depicted above from two molecules of butadiene involves the opening of two double bonds into single ones and the formation of a single bond in the middle of a hydrocarbon chain. If B is the energy required to convert a double into a single bond and A is the energy of the single bond, an amount $2B - A$ must be supplied to perform the necessary changes in the bonds. These are, however, not the only energies concerned, for the resonance energy $2R_B$ of two butadiene molecules must be supplied while at the same time the resonance energy R_D of the di-radical will become available. The energy of formation of the di-radical activated complex from two molecules of

butadiene is thus $2B - A + 2R_B - R_D$, and this must not be greater than the energy of activation of the reaction, *i.e.*, 23.7 kcal. The value of $B - A$ has been estimated from thermochemical data to be -24.5 kcal., and R_B and R_D have been calculated by the method of molecular orbitals to be 5 and 30 kcal., respectively; thus, A must be less than 93 kcal. Although there is some doubt as to the exact strength of a C—C bond in the middle of a hydrocarbon chain, it is definitely less than this figure, and so the formation of the di-radical appears possible.

On account of resonance in the di-radical the structure may be represented by the symmetrical configuration



In addition to the four degrees of translational freedom of the activated complex, there are three degrees of rotation and three of internal rotation about the 3-4, 4-5 and 5-6 bonds, respectively, leaving 50 degrees of vibrational freedom. The appropriate frequencies, which have been assessed by comparison with known frequencies of similar bonds in other molecules, together with the entropy contributions derived from the corresponding partition functions, are recorded in Table XXIV.

TABLE XXIV.—VIBRATION FREQUENCIES AND ENTROPIES OF DI-RADICAL

Type of vibration	Number	Frequency, cm. ⁻¹	Entropy, E.U.
H—C stretching.....	12	3,000	0.12
H—C—H bending.....	4	1,440	1.16
H—C—C bending.....	18	950	13.27
C—C stretching.....	2	1,000	1.34
C=C stretching.....	4	1,335	1.45
C—C—C bending.....	2	320	5.14
C—C=C bending.....	2	320	5.14
C=C=C bending.....	2	336	4.95
C=C torsion.....	2	190	7.20
C=C torsion.....	2	407	4.24

The total vibrational entropy is thus 44.0 E.U. per mole. The translational entropy is 43.7 E.U., and that due to internal

and external rotations, on the assumption of 1.40 Å. for the C=C bond distance and 1.53 Å. for the normal single-bond distance, is 51.4 E.U.; the latter value includes the contribution of the symmetry factor, *i.e.*, 2, and the estimated electron multiplicity, *i.e.*, 4, of the activated complex. The total entropy of the activated complex is thus 139.1 E.U. per mole at 1 atm. pressure. The entropy of two moles of butadiene is 177.6 E.U. under the same conditions, and so ΔS_p^\ddagger is -38.5, as recorded in Table II, page 23. By utilizing Eq. (176), page 199, it follows that for the bimolecular reaction, involving two molecules of butadiene to form a di-radical activated complex, the frequency factor A in the equation $k = A e^{-E_{\text{exp.}}/RT}$ is given by

$$A = 2e^2 \frac{kT}{h} e^{\Delta S_p^\ddagger/R} RT = 2.8 \times 10^{10} \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

at 600°K.; the factor 2 is introduced because the specific rate is given in terms of moles of butadiene and two molecules are concerned in the formation of the activated complex. This result is very close to that obtained experimentally and recorded at the beginning of this section. It may be mentioned that analogous calculations have been made for an assumed cyclic activated complex, but the frequency factor obtained in this manner is too low by a factor of about 10^3 .

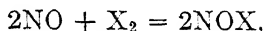
TERMOLULAR REACTIONS

Introduction.—Apart from the three-body collisions in which one atom or molecule carries off a large proportion of the energy liberated in the reaction between two other bodies, generally atoms or radicals, all the known gaseous reactions of the third order involve two molecules of nitric oxide. The interpretation of these reactions by means of the collision theory has been attempted,⁶⁶ but with little success; in the first place, the temperature coefficient of the reaction rate is negative in at least one case, *viz.*, the nitric oxide-oxygen reaction, and in the second place, the observed rates are considerably below the calculated values. The application of the theory of absolute reaction rates,

⁶⁶ L. S. Kassel, *J. Phys. Chem.*, **34**, 1777 (1930); "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., Inc., Chaps. IV and IX, 1932; C. N. Hinshelwood, "Kinetics of Chemical Change," Oxford University Press, 4th ed., Chap. VI, 1940.

however, gives a satisfactory explanation of the results in some of the termolecular reactions in which nitric oxide takes part.⁶⁷

Reactions Involving Nitric Oxide.—For a reaction of the type



where X is hydrogen, deuterium, oxygen, chlorine or bromine, the specific reaction rate according to the theory of absolute reaction rates is given by

$$k = \kappa \frac{g_{\ddagger}}{g_i} \frac{\frac{(2\pi m_{\ddagger} kT)^{3/2}}{h^3}}{\prod_3 \frac{(2\pi m_i kT)^{3/2}}{h^3}} \cdot \frac{\frac{8\pi^2(8\pi^3 ABC)^{1/2}(kT)^{3/2}}{h^3 \sigma_{\ddagger}}}{\prod_3 \left(\frac{8\pi^2 I_i kT}{h^2 \sigma_i} \right)} \cdot \frac{\prod_{11} (1 - e^{-h\nu_{\ddagger}/kT})^{-1}}{\prod_3 (1 - e^{-h\nu_i/kT})^{-1}} \cdot \frac{kT}{h} e^{-E_0/RT}, \quad (49)$$

where κ is the transmission coefficient, g_{\ddagger} and g_i are the electronic multiplicities of the activated and initial states, respectively, and σ_{\ddagger} and σ_i are the symmetry factors. The nuclear spin contributions are omitted since the reactions are not accompanied by any change in ortho-para ratio. In general the suffix i refers to the initial state and \ddagger to the activated complex; the three moments of inertia of the latter are indicated by A , B and C . The activated complex contains six atoms; and since there are three ordinary degrees of translational freedom and one degree of translation along the decomposition coordinate, the partition function will contain 11 vibrational terms; these are included in the numerator of the rate equation. The denominator is made up of the products of the partition functions for three diatomic molecules, and since these all have the same form the abbreviated method of formulation has been employed in Eq. (49). If those quantities which are functions of temperature are separated from the others, the latter being represented by G , Eq. (49) reduces to

$$k = G \frac{\prod_{11} (1 - e^{-h\nu_{\ddagger}/kT})^{-1} e^{-E_0/RT}}{\prod_3 (1 - e^{-h\nu_i/kT})^{-1} T^{7/2}}, \quad (50)$$

⁶⁷ H. Gershinowitz and H. Eyring, *J. Am. Chem. Soc.*, **57**, 985 (1935).

$$\therefore k \frac{\prod_{i=1}^3 (1 - e^{-h\nu_i/kT})^{-1}}{\prod_{\dagger} (1 - e^{-h\nu_{\dagger}/kT})^{-1}} T^{1/2} = G e^{-E_0/RT}, \quad (51)$$

the transmission coefficient κ being taken as unity. Upon taking logarithms and differentiating with respect to $1/T$, it is seen that

$$d(1/T) \ln \frac{\prod (1 - e^{-h\nu_i/kT})^{-1}}{\prod (1 - e^{-h\nu_{\dagger}/kT})^{-1}} T^{1/2} = -\frac{E_0}{R}; \quad (52)$$

and so if the quantity

$$\ln k + \ln \prod_{i=1}^3 (1 - e^{-h\nu_i/kT})^{-1} + \frac{1}{2} \ln T - \ln \prod_{\dagger} (1 - e^{-h\nu_{\dagger}/kT})^{-1} \quad (53)$$

is plotted against $1/T$, the slope of the resulting straight line should be $-E_0/R$. In this manner, E_0 may be evaluated from measurements of k at a series of temperatures.

Before proceeding to consider the quantitative application of the equations derived above, it is of interest to examine their qualitative implications. If the vibrations are all of fairly high frequency, the partition function $(1 - e^{-h\nu/kT})^{-1}$ is almost unity for all vibrational modes, and under these conditions Eq. (50) reduces to the form

$$k = \frac{G}{T^{1/2}} e^{-E_0/RT}. \quad (54)$$

It is evident that if E_0 is small or zero, the specific reaction rate will *decrease* with increasing temperature, as is actually found in the reaction between nitric oxide and oxygen. If E_0 is not small, but not too large, the rate constant will increase with temperature at low temperatures; but as the temperature is raised, k will reach a maximum and then start to decrease. The effect of the $T^{1/2}$ factor in the denominator is offset to some extent when the vibration frequencies are relatively low; the vibrational

partition function contribution then increases appreciably as the temperature is raised.

The Nitric Oxide-Oxygen Reaction.—In order to proceed with the calculation of the rate constant, it is necessary to know something of the configuration and vibration frequencies of the activated complex. The problem is too complicated to be dealt with by the methods of Chap. III, and so a reasonable structure must be postulated; for the reaction between two molecules of nitric oxide and one of oxygen the one depicted in Fig. 72 may be assumed as the basis of subsequent treatment. Since the oxygen atoms are held together by a single bond, free rotation about this bond will be possible,* so that the 11 vibrational modes of the activated state become 10 vibrations and 1 internal rotation, the partition function for the latter being (*cf.* page 263)

$$\frac{(8\pi^3 I_D kT)^{1/2}}{h}$$

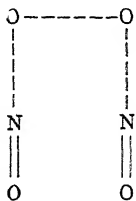


FIG. 72.—Assumed activated complex for the reaction between nitric oxide and oxygen.

where I_D is the moment of inertia of rotation about the O—O bond. The rate of reaction is given by an equation similar to (49), except that the partition function for one of the vibrational modes in the numerator is replaced by the contribution for internal rotation. It will be seen that the factor which is temperature-dependent in the new rate equation now contains T^3 , instead of $T^{1/2}$, so that the plot of the quantity

$$\ln k + \ln \prod_{i=1}^3 (1 - e^{-h\nu_i/kT})^{-1} + 3 \ln T - \ln \prod_{j=1}^{10} (1 - e^{-h\nu_j/kT})^{-1} \quad (55)$$

against $1/T$ gives $-E_0/R$. Upon substituting the numerical values for the universal constants and expressing molecular weights M in grams and moments of inertia in gram-Å.² per mole units, it is found that

* Since the two nitrogen atoms in N_2O_4 are joined by a valence bond, it is possible that there may be some attachment between these atoms in the activated complex: if this is so, there will be no free rotation in the molecule.

$$k = 1.6 \times 10^{19} \times \frac{g_{\ddagger}}{g_i} \cdot \frac{M_{\ddagger}^{-1/2}}{\prod M_i} \cdot \frac{(ABC)^{1/2} I_D^{1/2}}{\sigma_{\ddagger} \cdot \prod (I_i/\sigma_i)} \cdot \frac{\prod_{i=1}^{10} (1 - e^{-h\nu_i/kT})^{-1}}{3} \cdot \frac{1}{T^3} e^{-E_0/RT}; \quad (56)$$

$$\prod (1 - e^{-h\nu_i/kT})^{-1}$$

in cc.² mole⁻² sec.⁻¹ units. The vibration frequencies of the activated state may be expected to be similar to those of N₂O₄, and as a first approximation they will be assumed to be the same.⁶⁸ In the temperature range of interest, viz., 80 to 660°K., the effect of frequencies greater than 900 cm.⁻¹ is negligible; further, the

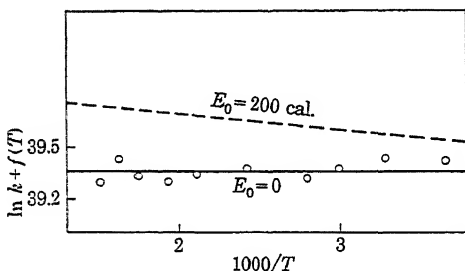


FIG. 73.—Derivation of the activation energy for the reaction between nitric oxide and oxygen.

lowest frequency is replaced by the free internal rotation in the complex, and so there are only seven vibrational frequencies of N₂O₄ that need be considered as applying to the activated state. These are 283, 380, 500, 600, 752, 813 and 813 cm.⁻¹ The vibration frequencies of nitric oxide and oxygen are so high that the respective partition functions are effectively unity; this has the effect of simplifying the expression for obtaining E_0 , and the quantity

$$\ln k + 3 \ln T - \ln \prod_{i=1}^7 (1 - e^{-h\nu_i/kT})^{-1} \quad (57)$$

when plotted against $1/T$ should be a straight line of slope $-E_0/R$. Upon introducing the seven frequencies given and utilizing the known values of k at different temperatures, the results shown in Fig. 73 are obtained; it is clear that E_0 is very

⁶⁸ G. B. B. M. Sutherland, *Proc. Roy. Soc.*, **141**, A, 342 (1933).

small or zero, for an activation energy as low as 200 cal. per mole would have given the slope of the line appropriately marked in the figure. The very small energy of activation may at first appear surprising, but when it is remembered that both nitric oxide and oxygen are paramagnetic, and so behave virtually as free radicals, the result does not seem unreasonable.

By introducing the approximation explained above for the vibrational partition functions in Eq. (56) and putting E_0 equal to zero, the rate equation becomes

$$k = \frac{g_{\ddagger}}{g_i} \left(\frac{M_{\ddagger}}{\prod_i M_i} \right)^{3/2} \frac{(ABC)^{1/2} I_D^{1/2}}{\sigma_{\ddagger} \prod_i (I/\sigma_i)} \prod_{i=1}^7 (1 - e^{-h\nu_i/kT})^{-1} \times \frac{1.6 \times 10^{19}}{T^3}. \quad (58)$$

The moments of inertia of the reacting molecules can be derived from spectroscopic measurements, but the evaluation of those of the activated complex requires a knowledge of its configuration and dimensions. The N=O and O—O distances in Fig. 72 are assumed to be 1.22 and 1.32 Å., which are close to the normal values, and the N—O separation is taken as 5 Å., by analogy with the H—H separation in the activated state for the combination of hydrogen atoms (see page 130). This figure, like the others and the vibrational frequencies, is not critical; the largest reasonable variations would not affect the final result by a factor of more than about 10. The free rotation about the O—O bond in the activated complex will have relatively little effect on the principal moments of inertia, and so the complex may be treated as a rigid molecule without incurring serious error. The symmetry numbers of oxygen and the activated complex are 2 in each case, while that for nitric oxide is unity. Upon introducing the moments of inertia in Eq. (58), the following result is obtained:

$$k = \frac{g_{\ddagger}}{g_i} \cdot \prod_{i=1}^7 (1 - e^{-h\nu_i/kT})^{-1} \times \frac{3.2 \times 10^{17}}{T^3} \text{ cc.}^2 \text{ mole}^{-2} \text{ sec.}^{-1} \quad (59)$$

where g_i is the product of the electronic multiplicities of the two molecules of nitric oxide and one of oxygen and g_{\ddagger} is that of the activated complex. These electronic statistical weights are derived from spectroscopic measurements; the normal state of nitric oxide is $^2\Pi$ and, the separation of the levels being taken into account, the statistical weight at ordinary temperatures is

3.1. The oxygen molecule is in a $^3\Sigma$ state, but as the three levels are very close together, the corresponding statistical weight may be taken as 3.0, so that g_i is $3 \times (3.1)^2$. The activated state lies somewhere between $2\text{NO} + \text{O}_2$, on the one hand, for which the electronic statistical weight would be the value in the initial state, i.e., $3 \times (3.1)^2$, and 2NO_2 on the other hand, when the statistical weight would be 4.* It follows, therefore, that g_{\ddagger}/g_i will be between unity and $4/[3 \times (3.1)^2]$, i.e., between 1 and 1/7.2. There is a possibility that the activated state may have the same electronic multiplicity as N_2O_4 , which is unity; under these circumstances, g_{\ddagger}/g_i would be $1/[3 \times (3.1)^2]$, i.e., 1/28.8; but as there seems no possibility of making an a priori decision as to the correct value of this factor, the intermediate result 1/7.2 will be used in the calculations. As these, in any case, cannot be exact within a factor of 10, the error, if any, will not be serious. The vibration frequencies of the activated state have been already given, and thus the data necessary for the calculation of the specific reaction rate are available; the results obtained, on the basis that the transmission coefficient is unity, are recorded in Table XXV, together with the experimental values for the same temperatures.⁶⁹

Comparison of the experimental and calculated rate constants shows satisfactory agreement, which lends support to the unexpectedly low activation energy as well as to the general method of treating reaction rates. The calculated values are seen to pass through a minimum at about 560°K ., and it is a very striking fact that such a minimum has been observed at 627°K . A slight revision of one vibration frequency would make these temperatures identical, without materially affecting the magnitude of the rate coefficient. As indicated above, the minimum is to be ascribed to the fact that as the temperature is raised the partition functions of the vibrational modes increase greatly and the resulting increase in the numerator of Eq. (58) eventually

* Each NO_2 molecule has one uncoupled electron so that the spin quantum number is $\frac{1}{2}$; two molecules may couple in the activated complex to give a resultant spin of 0 or 1. The multiplicities of these two states i.e., $2i + 1$, are thus 1 and 3, respectively; and hence the total is 4, provided that the energies of the triplet and singlet states are not very different.

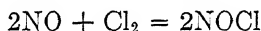
⁶⁹ E. Briner, W. Pfeiffer and G. Malet, *J. chim. phys.*, **21**, 25 (1924); M. Bodenstein *et al.*, *Z. Elektrochem.*, **24**, 183 (1918); *Z. physik. Chem.*, **100**, 87, 106 (1922).

overtakes the increase in the denominator resulting from the T^3 term.

TABLE XXV.—CALCULATED AND OBSERVED RATES FOR THE NO-O₂ REACTION

$T, ^\circ\text{K.}$	$k \times 10^{-3},$ cc. ² mole ⁻² sec. ⁻¹	
	Calc.	Obs.
80	86.0	41.8
143	16.2	20.2
228	5.3	10.1
300	3.3	7.1
413	2.2	4.0
564	2.0	2.8
613	2.1	2.8
662	2.0	2.9

The Nitric Oxide-Chlorine Reaction.—The reaction



can be treated in a manner essentially similar to that described above for nitric oxide and oxygen, the activated complex being assumed to have the configuration shown in Fig. 72 with a chlorine molecule replacing the oxygen molecule. The vibration frequencies cannot be fixed closely; but by analogy with the data on the spectra of similar molecules, the seven representative frequencies may be taken as 200, 300, 300, 500, 500, 700 and 700 cm.⁻¹ As before, the plot of the expression

$$\ln k + 3 \ln T - \ln \prod (1 - e^{-h\nu_i/kT})^{-1} \quad (60)$$

against $1/T$ is a straight line; from its slope, E_0 is estimated to be 4,780 cal. per mole. In the activated complex the Cl—Cl distance is taken as 2.5 Å., as in a partly dissociated chlorine molecule, and the N—Cl distance as 4 Å.; by using these figures the moments of inertia of the activated state can be estimated, and, upon inserting these together with the moments of inertia of nitric oxide and chlorine obtained from spectroscopic measurements, Eq. (58) becomes

$$k = \frac{g_{\ddagger}}{g_i} \prod (1 - e^{-h\nu_{\ddagger}/kT})^{-1} \times \frac{5.6 \times 10^{16}}{T^3} e^{-4,780/RT} \quad (61)$$

in cc.² mole⁻² sec.⁻¹ units. Since the chlorine molecule is normally in a singlet state, the limiting values of g_{\ddagger}/g_i are 1 and $4/(3.1)^2$; taking the former value, for simplicity, the rate coefficients given in Table XXVI are obtained, the assumption being made that the transmission coefficient is unity.

TABLE XXVI.—CALCULATED AND OBSERVED RATES FOR THE NO-Cl₂ REACTION

T, °K.	$k \times 10^{-6}$, cc. ² mole ⁻² sec. ⁻¹	
	Calc.	Obs.
273	1.4	5.5
333	2.2	9.5
355	8.6	27.2
401	18.3	72.2
451	25.4	182
506	64.7	453
566	120.2	1,130

The experimental data⁷⁰ are not very reliable, but it is evident that the calculated specific rates are within a factor of 5 to 10 of the observed values. Closer coincidence could be obtained by a different choice of frequencies for the activated state, but in the absence of more exact information the general agreement of the last two columns of the table may be regarded as providing support for the application of the theory of absolute reaction rates to termolecular reactions.

Other Termolecular Reactions.—There are not enough data for the nitric oxide-bromine reaction to permit the calculation of E_0 ; because of the heavier halogen atom the vibration frequencies will probably be lower than for the corresponding chlorine reaction, and so also will be the activation energy since the Br—Br bond is weaker than the Cl—Cl bond. It follows from Eq. (61), therefore, that the rate of the reaction between nitric oxide and bromine should be greater than that with

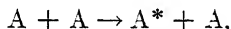
⁷⁰ M. Trautz *et al.*, *Z. anorg. Chem.*, **88**, 285 (1914); **97**, 241 (1916); **110**, 237 (1920); A. von Kiss, *Rec. trav. chim.*, **42**, 112, 665 (1923); **43**, 68 (1924).

chlorine at the same temperature; this deduction is in agreement with experiment.⁷¹

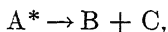
The reaction between nitric oxide and hydrogen has an apparent activation energy of about 47.0 kcal., and for such a high value the rate constant is much too large to be accounted for by the methods used above for the reactions involving nitric oxide with oxygen and chlorine. It is probable that the hydrogen reaction has a much more complex mechanism than the others.⁷² In view of the similarity between nitric oxide and oxygen, both being paramagnetic, and the complexity of the hydrogen-oxygen reaction, a relatively complicated mechanism for the nitric oxide-hydrogen reaction, perhaps involving chains, would not be unexpected.

UNIMOLECULAR REACTIONS

Collision Treatment.—According to the collision theory of unimolecular reactions⁷³ (see page 9), the reacting molecule acquires its energy of activation in several degrees of freedom by collision with another molecule; thus,



where A^* represents the activated molecule. If c_A is the concentration of A molecules, then the rate of formation of activated molecules is given by $k_1 c_A^2$, where k_1 is the specific rate of the activation process. A certain minimum amount of the energy so acquired must pass into one or more of the bonds that have to be broken if the molecule is to decompose; thus,



so that the rate of reaction is $k_2 c_{A^*}$, where c_{A^*} is the concentration of the activated molecules and k_2 is the rate constant. In the interval elapsing between activation and decomposition, the activated molecule may become deactivated as the result of a collision with an A molecule; the rate of deactivation is thus

⁷¹ M. Trautz and V. P. Dalal, *Z. anorg. Chem.*, **102**, 149 (1918).

⁷² C. N. Hinshelwood and T. E. Green, *J. Chem. Soc.*, **129**, 720 (1926); J. W. Mitchell and C. N. Hinshelwood, *ibid.*, 378 (1936).

⁷³ F. A. Lindemann, *Trans. Faraday Soc.*, **17**, 599 (1922); see also Hinshelwood, Ref. 66, Chap. V.

$k'_1 c_A^* c_A$. In the stationary state the rate of formation of activated molecules is equal to the sum of the rates of decomposition and deactivation; *i.e.*,

$$k_1 c_A^2 = k_2 c_A^* + k'_1 c_A^* c_A, \quad (62)$$

so that the rate of reaction is given by

$$-\frac{dc_A}{dt} = k_2 c_A^* = \frac{k_1 k_2 c_A^2}{k'_1 c_A + k_2} \quad (63)$$

This is the equation for a reaction of order between 1 and 2; if c_A is large, *i.e.*, at relatively high pressures, and the rate of deactivation $k'_1 c_A^* c_A$ is large in comparison with the rate of decomposition $k_2 c_A^*$, *i.e.*, if k_2 may be neglected in comparison with $k'_1 c_A$, Eq. (63) becomes

$$\frac{dc_A}{dt} = \frac{k_1 k_2}{k'_1} c_A. \quad (64)$$

Under these conditions the reaction is consequently kinetically of the first order. At low pressures, when c_A is small, the rate of deactivation is small in comparison with the rate of decomposition; *i.e.*, $k'_1 c_A^* c_A$ in Eq. (62) can be neglected in comparison with $k_2 c_A^*$. Equation (63) then reduces to

$$\frac{dc_A}{dt} = k_1 c_A^2, \quad (65)$$

so that the reaction becomes of the second order. This change from first- to second-order kinetics as the pressure is lowered has been observed in a large number of cases, and the results have been taken as providing general support for the theory outlined above. As long as the process is first order, the time to complete a certain fraction of the reaction is independent of the pressure; but as it approaches second-order behavior, the rate of change falls off with decreasing pressure.

Suppose that an apparent unimolecular rate coefficient k_{uni} , which is not a constant at all pressures, is defined by the expression

$$\text{Rate of reaction} = -\frac{dc_A}{dt} = k_{\text{uni}} c_A. \quad (66)$$

It follows, therefore, from Eq. (63) that

$$k_{\text{uni.}} = \frac{k_1 k_2 c_A}{k_1' c_A + k_2}, \quad (67)$$

$$\therefore \frac{1}{k_{\text{uni.}}} = \frac{k_1'}{k_1 k_2} + \frac{1}{k_1 c_A}. \quad (68)$$

The plot of $1/k_{\text{uni.}}$, obtained from the experimental data, against $1/c_A$ should give a straight line; but in actual fact this is not quite true, as shown in Fig. 74.* This result has been explained

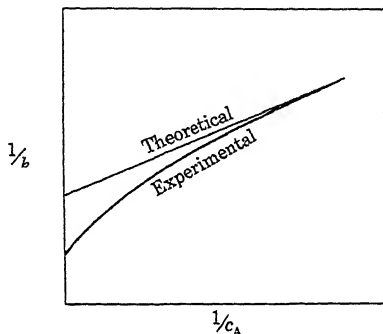


FIG. 74.—Theoretical and experimental specific rates of unimolecular reaction.

in terms of the collision theory by postulating that k_2 , the specific rate of the decomposition of the activated molecules, is not constant but depends on the energy these molecules have in excess of a certain minimum value. Before discussing this subject, it is necessary to consider another aspect of the collision theory.

Mention has already been made (page 9) of the fact that the frequency factor for unimolecular reactions is often much larger than that given by the simple collision theory. This difficulty was overcome by the suggestion that, since most unimolecular processes involve relatively large molecules, several (n) square terms can contribute to the energy of activation.⁷⁴

* The figure is frequently drawn in such manner as to indicate that the theoretical and experimental curves become asymptotic at high pressures, *i.e.*, when $1/c_A$ is small; this is, however, misleading, for it suggests that at low pressures the rate constant is greater than would be expected from the simple theory, whereas it is probably the same.

⁷⁴ C. N. Hinshelwood, *Proc. Roy. Soc.*, **113**, A, 230 (1926); R. H. Fowler and E. K. Rideal, *ibid.*, **113**, A, 570 (1927); *cf.* G. N. Lewis and D. F. Smith *J. Am. Chem. Soc.*, **47**, 1508 (1925).

The probability that a molecule will have energy E is now much larger than $e^{-E/RT}$, and the rate of reaction is given, as a first approximation, by the expression

$$k = Z \frac{(E/RT)^{\frac{1}{2}n-1}}{(\frac{1}{2}n-1)!} e^{-E/RT} \quad (69)$$

where Z is, as before, the collision number (page 5). By choosing a suitable value for n , it is possible to fit the experimental data; in general, the number of degrees of freedom required to account for the results is consistent with the known size of the molecule. It may be pointed out that Eq. (69) is applicable only when there is an equilibrium between normal and activated molecules; *i.e.*, it can hold only in the high-pressure region and so must not be used when the rate shows an appreciable falling off.

According to the development of the theory by O. K. Rice and H. C. Ramsperger⁷⁵ and by L. S. Kassel,⁷⁶ it is supposed that the rate constant k_2 is a function of the actual energy possessed by the molecule in its various degrees of freedom; the larger this energy, the greater the probability that the requisite amount will pass into a given bond and hence the greater will be the specific rate of the decomposition reaction. The statistical weight of a system of s degrees of vibrational freedom containing j quanta of vibrational energy is equal to the number of ways in which j objects can be divided among s boxes, each of which may contain any number; the number of different configurations is

$$\frac{(j+s-1)!}{j!(s-1)!}.$$

The statistical weight for states in which the s oscillators have j quanta among them and some particular one has m quanta is similarly found to be

$$\frac{(j-m+s-1)!}{(j-m)!(s-1)!}.$$

⁷⁵ O. K. Rice and H. C. Ramsperger, *ibid.*, **49**, 1617 (1927); **50**, 617 (1928).

⁷⁶ L. S. Kassel, *J. Phys. Chem.*, **32**, 225 (1928); "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., Inc., Chap. V, 1932. See also E. Patat, *Z. Elektrochem.*, **42**, 85 (1936).

It follows, therefore, that the probability for a particular oscillator to have m quanta when all s oscillators possess j quanta is the ratio of these quantities; *i.e.*,

$$\frac{(j - m + s - 1)! j!}{(j - m)!(j + s - 1)!} \approx \left(\frac{j - m}{j}\right)^{s-1}, \quad (70)$$

if j is very large. The rate at which the required energy gets into the particular degree of freedom is proportional to this probability, and so k_2 is also proportional to it; thus,

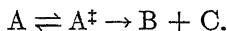
$$k_2 = k'_2 \left(\frac{j - m}{j}\right)^{s-1}. \quad (71)$$

The total number of quanta j may be taken as proportional to E , the total energy possessed by the molecule, whereas m is proportional to the minimum requisite energy E_0 that the bond must have prior to decomposition; it follows, therefore, that

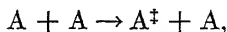
$$k_2 = k'_2 \left(\frac{E - E_0}{E}\right)^{s-1}. \quad (72)$$

Since all the energies from E_0 to infinity are possible, it is necessary to integrate between these limits; this has been done graphically, on the assumption of a Maxwell-Boltzmann distribution of energies, and it has been shown that by choosing reasonable values of s it is possible to account for the experimental results.

Theory of Absolute Reaction Rates.—It was seen in Chap. I that the large frequency factors of unimolecular reactions can if necessary be accounted for by the statistical treatment of reaction rates. It is of interest, therefore, to see whether or not the general ideas of the theory of absolute reaction rates can be extended to cover other aspects of the problem of unimolecular reactions. In the reaction $A = B + C$, the system must pass through the activated complex A^\ddagger which is the same for both forward and back reactions; thus,



When two molecules of A collide in such a manner that sufficient energy passes into the appropriate bond or bonds, one of the molecules may form the activated complex of the reaction; thus,



and at reasonably high pressures there will be a sufficient number of collisions for the equilibrium concentration of A^\ddagger to be maintained. By following the treatment of Chap. IV, the equilibrium constant, for the system involving the initial and activated states, may be expressed as

$$K = \frac{c_A c_{\ddagger}}{c_A^2} = \frac{c_{\ddagger}}{c_A} = \frac{F_{\ddagger}'}{F_A}; \quad (73)$$

$$c_{\ddagger} = c_A \frac{F_{\ddagger}'}{F_A} \quad (74)$$

where the symbol \ddagger refers to the activated state. By Eq. (132), Chap. IV,

$$\text{Rate of reaction} = c_{\ddagger} \left(\frac{kT}{2\pi m^*} \right)^{1/2} \frac{1}{\delta} \quad (75)$$

$$= c_A \frac{F_{\ddagger}'}{F_A} \left(\frac{kT}{2\pi m^*} \right)^{1/2} \frac{1}{\delta} \quad (76)$$

$$= c_A \frac{F_{\ddagger}}{F_A} \cdot \frac{kT}{h} e^{-E_0/RT}, \quad (77)$$

where F_{\ddagger} is, as before, the partition function for unit volume, the contribution of the degree of freedom along the coordinate of decomposition being excluded; the zero-point factors have been eliminated from the partition functions in the usual manner. It is seen from Eq. (77) that the reaction rate is proportional to the first power of the concentration of the reactant A; hence, the process will be kinetically of the first order, provided that the fundamental assumption implied in Eq. (75), that passage over the energy barrier determines the rate of reaction, is correct. The reaction is of the first order, in spite of the fact that activation involves collision between two molecules, because the activated state consists of the single molecule A^\ddagger and not of the double molecule A_2^\ddagger .

Transmission Coefficient in Unimolecular Reactions.—In this treatment, no account has yet been taken of the transmission coefficient; this, however, plays an important part in unimolecular reactions and so must be given consideration. If the reaction is of the type postulated above, *i.e.*, the type in which a molecule of A dissociates into B and C, there are two stages that might be rate-determining: (1) the activation process involving the transfer of energy of the colliding molecules into

energy in the correct degree of freedom in the activated complex,* and (2) passage of the activated complex over the potential barrier, resulting in decomposition. This is equivalent to saying either that the specific rate constant k_1 may be small in comparison with k_2 or that k_2 may be small relative to k_1 , respectively; the symbols k_1 and k_2 have virtually the same significance as on page 281. If the energy-transfer process is rapid, as it generally will be at fairly high pressures, k_2 will be relatively small; and if it is neglected in comparison with $k'_1 c_A$ in Eq. (63), the result is the same as Eq. (64). The reaction will be of the first order, and the velocity will depend on the rate at which activated complexes cross the barrier; Eq. (77) and the equations in Chap. I will then be applicable, with the transmission coefficient approximately unity.

As the pressure is decreased, the number of activating collisions, which is proportional to the square of the pressure of the gas, diminishes more rapidly than the rate of passage over the barrier, and so the transfer of energy will become rate-determining. The consequence is that it is necessary to introduce a transmission coefficient which is less than unity and whose value depends on the pressure. Since the transmission coefficient κ of both forward and reverse reactions must be the same (see page 216), the necessary information concerning κ can be obtained from a consideration of the reverse reaction. If two particles, atoms or molecules, B and C come together with sufficient energy to form A^\ddagger , the resultant will be stabilized only if there is available another substance, *e.g.*, a molecule of A, to remove the excess energy. An extreme case of this type occurs when two hydrogen atoms associate; as seen on page 215, the transmission coefficient may then be as small as 10^{-14} in the absence of a third body. If ν_c is the frequency of collisions between the activated molecules A^\ddagger and normal molecules A, and α_c is the probability of deactivation occurring on collision, the transmission coefficient for the process under consideration may be written

$$\kappa = \frac{\alpha_c \nu_c}{A + \alpha_c \nu_c}, \quad (78)$$

* The possibility that under certain conditions the redistribution of energy among internal degrees of freedom becomes rate-determining is considered later.

where A is the frequency factor of the reaction, which may be put equal to kT/h . This relationship gives the fraction of the total number of systems crossing the energy barrier, *i.e.*, $A + \alpha_c \nu_c$, in unit time that become deactivated and hence yield A molecules. Since ν_c depends on the pressure of the gas, it is evident that a transmission coefficient of this type, which applies also to the direct reaction, *i.e.*, $A \rightarrow B + C$, is pressure-dependent. It is apparent that at low pressures k_1 and k'_1 (page 281) will be small, since the κ included in both of them will be much less than unity; under these conditions, $k'_1 c_A$ in Eq. (63) can be neglected in comparison with k_2 , and Eq. (65) results. The unimolecular process should thus become of the second order at low pressures.

As long as the reactant A decomposes into two, or more, molecules of product, there is very little possibility of the activation energy returning to the bond that was broken in the reaction. In the case of isomeric change, however, there is only one molecule of product, and unless the energy of the activated molecule is transferred rapidly to the various internal degrees of freedom of the product, and subsequently removed by collisions with other molecules, the energy may return to the point of reaction and the process will be reversed. If the slow stage is the transfer of energy from internal degrees of freedom to translational energy of a colliding molecule, the treatment of the transmission coefficient is similar to that already given; this is apparently the case in the low activation energy *cis-trans* isomerization processes at low pressures (page 329). The transmission coefficient and the specific rate depend on the total pressure. On the other hand, if the transfer of energy between internal degrees of freedom is rate-determining,⁷⁷ the transmission coefficient will be given approximately by the equation

$$\kappa = \frac{\sum_{i=1}^m \alpha_i \nu_i}{A + \sum_{i=1}^m \alpha_i \nu_i}, \quad (79)$$

where ν_i is the frequency of "internal collisions," *i.e.*, the frequency with which the possibility of transfer of energy to other

⁷⁷ Cf. E. A. Guggenheim and J. Weiss, *Trans. Faraday Soc.*, **34**, 57 (1938).

degrees of freedom occurs, and α_i is the probability of transfer per internal collision for the i th degree of freedom, there being a total of m such degrees of freedom. Since ν_i does not depend on the pressure, it follows that in these circumstances κ will not vary with the total pressure of the reacting system. Such a condition apparently exists in the cis-trans isomerizations requiring high activation energies (page 331). It may be remarked that the three cases considered here are extremes, and conditions may, and no doubt frequently do, arise in which none of the three processes mentioned is completely rate-determining; the behavior is then intermediate between the types discussed above.

When the circumstances are such that the slow stage of a reaction involves transfer of energy, the activated molecules may no longer be regarded as being in equilibrium with the bulk of the reactant. The problem of calculating the net rate of passage of systems over the energy barrier should then be treated quantum mechanically by the methods employed in the study of cis-trans isomerization,⁷⁸ although another possible approach is outlined on page 327.

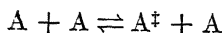
Quite apart from the nature of the rate-determining step, the transmission coefficient of a unimolecular reaction may be low if the process is nonadiabatic in nature and involves the crossing of potential-energy surfaces. It is possible, although not definitely established, that the low frequency factor for the thermal decomposition of nitrous oxide can be accounted for in this manner (page 336). The small transmission coefficient found experimentally, even at high pressures, for the low activation energy cis-trans isomerization has also been explained by the aid of considerations based on the crossing of potential-energy surfaces (page 328).

Transfer of Energy.—It is necessary now to consider the mechanism by which the molecules of reactant acquire an adequate amount of energy in the correct degree of freedom, for as just seen this may become the rate-determining stage of the reaction at low pressures. Some information on this subject can be obtained by considering the efficiencies of various atoms or molecules in removing the excess energy of association reactions; it was seen in Chap. III that the hydrogen molecule formed

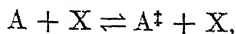
⁷⁸ J. L. Magee, W. Shand and H. Eyring, *J. Am. Chem. Soc.*, **63**, 677 (1941).

by the combination of two atoms could be stabilized only if some of the vibrational energy was removed as kinetic, or other, energy by collision with another atom or molecule. According to the potential-energy surfaces (Figs. 24 and 25) the reverse process, *viz.*, the conversion of kinetic energy of one molecule into vibrational energy of another, is equally possible. It appears, therefore, that the molecule of reactant undergoing unimolecular decomposition may acquire its energy as the result of the transfer and rearrangement of energy on collision. This point of view is supported by the fact that certain gases are particularly effective in maintaining the high pressure rate of a unimolecular reaction. For example, in the presence of hydrogen the rates of decomposition of propionaldehyde and other aldehydes and of ethers remain high even when the partial pressures of the reactant have fallen to a considerable extent. The addition of nitrogen or of helium, on the other hand, has only a relatively small influence on the falling off of the reaction rate observed at low pressures. The effect of added gases has been studied in various unimolecular reactions, and it has been found that no amount of the gas can increase the specific rate to a value greater than its limiting value at high pressures. It appears, therefore, that the added molecules do not interfere with the over-all chemical reaction and that their function is to maintain the equilibrium concentration of activated molecules. It may be mentioned, however, that the added substances which are most effective in this connection are those having some tendency to interact with the dissociating molecule (*cf.* page 115); this matter will be considered shortly in some detail.⁷⁹

The relative efficiencies of various molecules in transferring energy into the degree or degrees of freedom required to form the activated complex may be derived in the following manner: Suppose that the unimolecular decomposition of A proceeds in the presence of a foreign substance X with which, under the conditions of the experiment, it does not react appreciably; the formation of activated complexes can then occur in the equilibrium process

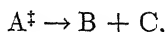


and



⁷⁹ *Cf.* J. Franek and A. Eucken, *Z. physik. Chem.*, **B**, 20, 460 (1933).

for which the forward rates are k_1 and k_x and the rates of the reverse reactions are k'_1 and k'_x , respectively. The decomposition of the activated complex, thus,



then takes place with the specific rate k_2 , as before. By a treat-

TABLE XXVII.—RELATIVE EFFICIENCIES OF GASES IN TRANSFERRING ENERGY IN UNIMOLECULAR DECOMPOSITION

Added gas	F ₂ O(250°C.)	N ₂ O(653°C.)	Azomethane (310°C.)
He	0.40	0.66	0.07
A	0.82	0.20
Kr	0.18
SiF ₄	0.88
N ₂	1.01	0.24	0.21
O ₂	1.13	0.23
F ₂	1.13
CO	0.13
CH ₄	0.20
CO ₂	1.32	0.25
H ₂ O	1.5	0.46
D ₂	0.46

ment analogous to that given previously (page 281), it is readily found that

$$-\frac{dc_A}{dt} = k_2 c_{A^\ddagger} = k_2 \frac{k_1 c_A^2 + k_x c_A c_X}{k'_1 c_A + k'_x c_X + k_2} \quad (80)$$

From the variation of the reaction rate with changes in the concentration of X and A, *i.e.*, in c_X and c_A , it is possible to calculate the values for k_x , representing the effectiveness of X molecules in transferring energy in collisions; this may be compared with k_1 for the efficiency of the A molecule itself. Some of the results for k_x/k_1 obtained in the unimolecular decomposition of fluorine monoxide,⁸⁰ nitrous oxide⁸¹ and azomethane⁸² are given in Table XXVII.

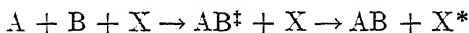
⁸⁰ W. Koblitz and H. J. Schumacher, *ibid.*, **B**, 25, 283 (1936.)

⁸¹ M. Volmer *et al.*, *ibid.*, **B**, 19, 85 (1932); **B**, 21, 257 (1933); **B**, 25, 81 (1934).

⁸² D. V. Sickman and O. K. Rice, *J. Chem. Phys.*, **4**, 608 (1936).

The data show that there is nothing specific about molecules of the same type as those undergoing decomposition, and in fact in some instances the foreign gas is even more effective in maintaining the equilibrium concentration of activated molecules. The efficiency for the transfer of energy is, on the whole, least for the inert gases; this is to be expected, in accordance with the discussion on page 115, since they have no tendency to combine chemically with the reacting substances.

If the property possessed by foreign gases of maintaining the equilibrium concentration of activated complexes, and thus preventing the falling off in rate of a unimolecular reaction, is to be attributed to their ability to transfer some of their energy to vibrational energy of the reacting molecule, then some parallelism is to be expected between their efficiency in this respect and for the removal of excess vibrational energy in association reactions. The same potential-energy surface is applicable for the association process



as for the reverse unimolecular reaction



where X^* represents a foreign molecule with a relatively large amount of translational energy.[†] It follows, therefore, that the ability of a foreign molecule to bring about exchange of translational for vibrational energy in a given molecule must operate in both directions. It is thus of interest to examine the relative efficiencies of various gases in facilitating the combination of halogen atoms; the experimental results are given in Table XXVIII.⁸²

It is seen that as in Table XXVII the inert gases have the smallest efficiencies, as is to be expected. An exact parallelism between the results for the efficiency of transfer of energy in the two opposite directions is, of course, not to be expected unless the same reaction were under consideration in both cases. The

[†] If X is an atom, the energy will be purely translational; but if it is a molecule, the excess energy can be in other degrees of freedom to some extent.

⁸² E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **31**, 689 (1935); **32**, 907 (1936); *J. Chem. Phys.*, **4**, 497 (1936).

general similarity between the results in Tables XXVII and XXVIII is sufficient to be of definite significance.

TABLE XXVIII.—RELATIVE EFFICIENCIES OF GASES IN CATALYZING THE COMBINATION OF HALOGEN ATOMS

	He	A	H ₂	N ₂	O ₂	CH ₄	CO ₂
Bromine.....	1.00	1.68	2.85	3.25	4.10	4.65	7.15
Iodine.....	1.00	1.94	2.16	3.60	5.67	6.57	9.85

Another aspect of the transfer of energy in molecular collisions is found in connection with the influence of foreign gases on the dispersion of sound at high frequencies. The dependence of the velocity on the frequency is attributed to the slow rate of exchange of energy between external, *i.e.*, translational, and internal, *i.e.*, vibrational, degrees of freedom. The influence of a foreign gas in preventing dispersion of the velocity of sound is consequently regarded as a measure of its efficiency in transferring energy. Some experimental values of these efficiencies, relative to those of the gases in which the velocity of sound is being studied, are given in Table XXIX.⁸⁴

TABLE XXIX.—RELATIVE EFFICIENCIES OF GASES IN TRANSFERRING ENERGY FROM DISPERSION OF SOUND DATA

Added gas	Chlorine	Nitrous oxide	Carbon dioxide
N ₂	0.88
A	1.1	1.0
He	33.3	3.3	33.3
D ₂	12.5
H ₂	50	9.1	125
CO	107	1.6
CH ₄	200	6.7	25
HCl	200	500
NH ₃	12.5
H ₂ O	2,000

Although the inert gases are still relatively ineffective, the influence of helium is sometimes greater than might be anticipated; nevertheless, when there is a tendency for reaction to

⁸⁴ A. Eucken, *Oester. Chem.-Ztg.*, 1 (1935); see O. Oldenberg and A. A. Frost, *Chem. Rev.*, 20, 99 (1937); E. Patat, *Z. Elektrochem.*, 42, 265 (1936).

occur between the foreign gas and that in which the velocity of sound is being measured, the efficiency of the former is relatively high. It should be noted that some discrepancy between the results from the dispersion of sound and those from the rate of chemical reaction is not unexpected, for in the former case the temperatures are so low that most molecules are in low energy states. The systems concerned are thus to be represented by mass points moving far down the potential-energy valleys, and unless the reactivity of the foreign gas is very high the surface will not be bent to any considerable extent in this region. The general relationship between efficiency of energy transfer under these conditions and reactivity found at high temperatures may thus be less clearly marked here.

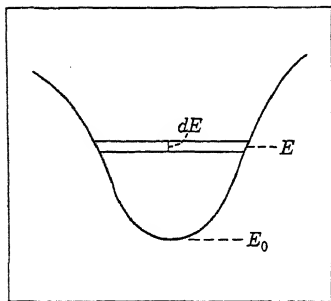


FIG. 75.—Cross section of potential-energy surface at saddle point.

In the simplest case of the approach of an atom or molecule X to a diatomic molecule AB, a transfer of energy takes place when the molecules are sufficiently close for the system to be in the curved region of the potential-energy surface. The molecule AB now becomes excited vibrationally, and X loses an equivalent amount of energy, which must be exclusively translational if X is an atom. In the case of a polyatomic reacting molecule the vibrational energy has to go into one or two particular bonds, of the many possible, before the activated complex can be formed. It would be necessary, in these circumstances, to use a many-dimensional potential-energy surface and to consider the curvature in the region corresponding to the bond in question. It may be inferred, from this argument, that the effect of a foreign gas would be related to its reactivity with the particular bond which has to be broken, rather than with the molecule as a whole.

From the present point of view the rate of activation, which determines the over-all rate of the reaction in the low-pressure region, may be expected to be a function of the total energy of the colliding system. The greater this energy, the more easily will the system be able to find its way to the activated state. The probability of activation will depend on the width of the gap,

corresponding to the energy E , through which the system has to pass. Suppose that Fig. 75 represents a cross section of the potential-energy surface at the saddle point, and let E_0 be the minimum energy necessary for the formation of the activated state. The width of the gap is related to the energy difference between E and E_0 , and this may be represented by an expression of the form $(E - E_0)^n$; for low values of $E - E_0$, when the vibrations are harmonic, n is 0.5, but it increases as E increases. The probability P of activation, which is one of the factors involved in the rate constant k_1 on page 281, is thus given, in general, by

$$P \propto (E - E_0)^n dE \quad (81)$$

for an energy between E and $E + dE$. The total probability for a molecule of energy between E_0 and E is thus given by

$$\int_{E_0}^E (E - E_0)^n dE \propto (E - E_0)^{n+1}, \quad (82)$$

which may be compared with Eq. (72) on page 285. In order to determine the rate of formation of activated complexes and hence the rate of the reaction, it would be necessary to integrate the probability $(E - E_0)^n dn$ over all energies between E_0 and infinity; since nothing is known of the distribution of energies in the nonequilibrium condition or of the value of n over an energy range, it does not seem possible, however, to make a quantitative test of the result without introducing some fundamental assumptions.

Entropy Changes in Unimolecular Reactions.—Since the rate of a unimolecular reaction can be expressed as kc_A , where k is the specific reaction rate, it follows from Eq. (77) that

$$k = \frac{kT}{h} \cdot \frac{F^\ddagger}{F_A} e^{-E_0/RT} \quad (83)$$

$$= \frac{kT}{h} K^\ddagger \quad (84)$$

$$= \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}, \quad (85)$$

and if ΔH^\ddagger is replaced by the experimental activation energy, Eq. (85) becomes [cf. Eq. (177), page 199]

$$k = ke \frac{kT}{h} e^{-E_{\text{exp}}/RT} e^{\Delta S^\ddagger/R}, \quad (86)$$

the transmission coefficient κ , previously omitted, being now included. It was stated in Chap. I that the activated complex in a unimolecular reaction may be expected to resemble the initial state; and hence the entropy of activation should, in general, be small. An alternative way of stating this conclusion is that the frequency factor A should be of the order of 10^{13} to 10^{14} sec.⁻¹ It should be noted that since the specific rate of a unimolecular reaction is independent of the concentration units, these are not mentioned in connection with the frequency factor, and further that the value of ΔS^\ddagger is independent of the standard state (see page 199). Although it appears from recent work that simple unimolecular reactions, free from chains or other complications, are rare, the results in Table XXX⁸⁵ may be taken as being in accordance with expectation.

TABLE XXX.—ENTROPY CHANGES IN UNIMOLECULAR GAS REACTIONS

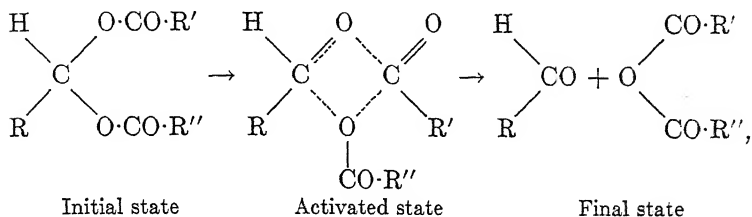
Decomposition of	Temp., °K.	A , sec. ⁻¹	E , kcal.	ΔS^\ddagger , E.U.
N ₂ O ₅	300	4.8×10^{13}	24.7	-2.5
CH ₃ ·O·CH ₃	780	1.6×10^{13}	58.5	2.5
<i>n</i> -C ₃ H ₇ ·O·NO	500	2.7×10^{14}	37.7	3.0
CH ₃ ·N ₃	500	3.0×10^{15}	43.5	8.2
C ₂ H ₅ I	550	1.8×10^{13}	43.0	-1.2
CH ₃ ·N:N·CH ₃	600	8.0×10^{15}	50.0	10.8
(CH ₂) ₂ O	700	6.3×10^{14}	52.0	5.5
SiMe ₄	950	1.7×10^{14}	78.8	2.2

In the calculation of the ΔS^\ddagger values in Table XXX, it has been assumed that the transmission coefficient κ is unity; the reaction rates seem to be so high that this approximation is justifiable. In many cases, however, frequency factors of the order of 10^{10} or less have been observed; these low values are often due to small transmission coefficients, for the reasons explained on page 287, but in other instances it is possible that the process of activation may be accompanied by an appreciable decrease of entropy. For example, in the decomposition of ethylidene diacetate, and of other esters of the general formula R·CH(O·CO·R)₂,⁸⁶ entropies of activation of -10 to -18 E.U. have been calculated

⁸⁵ Data from H. J. Schumacher, "Chemische Gasreaktionen," T. Steinkopf, 1938; Patat, Ref. 84.

⁸⁶ C. C. Coffin, *Can. J. Res.*, **5**, 636 (1931); **6**, 417 (1932).

on the assumption that the transmission coefficient is unity. In these reactions the activated complexes may contain more bonds than the original molecules, thus,



so that three degrees of internal rotation in the initial state have become vibrations in the activated state. Such a change will be accompanied by a decrease of entropy; this is, of course, in accord with the greater restriction to movement in the activated complex than in the molecule of reactant. It is of interest to mention that reactions which involve the breaking of a ring,⁸⁷ and which may consequently be regarded as the reverse of the decomposition of ethylidene diacetate type of reaction, are accompanied by a relatively large increase of entropy. The value of ΔS^\ddagger for the decomposition of ethylene oxide and of trioxymethylene are +7.5 and +17.5 E.U., respectively. High entropies of activation in certain reactions involving the formation of methyl radicals, *e.g.*, decomposition of azomethane, are attributed to the large amounts of rotational energy of the methyl radicals.

⁸⁷ H. C. Ramsperger, *J. Am. Chem. Soc.*, **49**, 912, 1495 (1927); O. K. Rice and H. Gershinowitz, *J. Chem. Phys.*, **3**, 479 (1935).

CHAPTER VI

REACTIONS INVOLVING EXCITED ELECTRONIC STATES

Photochemical Reactions.—The reactions considered hitherto involve atoms and molecules that remain in their lowest electronic states; reaction may thus be regarded as being restricted to one potential-energy surface. This is actually the lowest of a number of surfaces, but the others are so high that they make no appreciable contribution to the reaction. In photochemical processes, however, the reacting system acquires electronic energy as a result of the absorption of radiation, and so is raised to a higher level; this acquisition of energy is generally accompanied by dissociation of the absorbing molecule, which may occur directly or indirectly. The atoms or radicals resulting in this manner then undergo reactions that are determined by purely thermal considerations, such as have been discussed in the earlier chapters. The kinetics of the photochemical hydrogen-bromine reaction are, for example, fundamentally the same as those of the thermal reaction, although in the former case bromine atoms are produced by the absorption of the appropriate radiation, whereas in the latter they result from the dissociation of molecular bromine at elevated temperatures. In general, therefore, the theory of reaction rates offers little that is new in connection with photochemical reactions; the primary step, *i.e.*, the result of light absorption, is best studied by the aid of spectroscopy, and the subsequent stages are amenable to treatment by the theory of absolute reaction rates in the same way as for any other reactions.

Efficiency of Radiationless Transitions.¹—By means of the second law of thermodynamics, it is possible to derive certain restrictions concerning the efficiency of excitation of normal or excited atoms or molecules by ordinary thermal collision processes. Consider one mole of mercury atoms, *i.e.*, N atoms, in the excited 6^3P_0 state dispersed in a foreign gas; the difference E_1

¹ M. G. Evans, H. Eyring and J. F. Kincaid, *J. Chem. Phys.*, **6**, 349 (1938).

between the energy of this state and that of the normal 6^1S_0 state is almost entirely free energy. Suppose a number N_1 of the excited mercury atoms are raised by thermal collisions to the still higher 6^3P_1 state, where the energy referred to the ground state is E_2 . In such a process an amount of energy $N_1(E_2 - E_1)/N$ is converted from thermal energy of the molecules of the inert gas to the free energy of excitation of the mercury. This increase of free energy of part of the atoms must be balanced by a decrease, at least equal in amount, caused by radiationless transitions from the first excited level to the ground state of the other mercury atoms. The decrease in free energy, caused by N_2 such transitions, is given by $N_2(E_1/N)$;^{*} and hence $N_1(E_2 - E_1)/N$ must be equal to or less than this quantity. Since N is the sum of N_1 and N_2 , it follows that

$$\frac{N_1}{N} \leq \frac{E_1}{E_2} \quad \text{and} \quad \frac{N_2}{N_1} \geq \frac{(E_2 - E_1)}{E_2}$$

It is seen, therefore, that the second law of thermodynamics places an upper limit on the efficiency of excitation by radiationless transitions; and it follows that the number of quanta of energy, E_2/N , that can be emitted is restricted in the same way.

Chemiluminescence.—In photochemical processes a chemical change is initiated by the absorption of radiation; there is an interesting type of reaction in which the reverse occurs, *viz.*, in which a chemical change is accompanied by the emission of radiation in the form of light. Such reactions are said to exhibit "chemiluminescence"; they involve two or more potential-energy surfaces, and under certain conditions a transition from a lower to an upper surface can take place. Having found its way to the upper surface the resultant system, after the occurrence of a chemical change, can return to the lower surface with the emission of radiation; it is this radiation which constitutes chemiluminescence. Two simple types of behavior may be considered,

^{*} In reactions that do not involve a new kind of molecule, no concentration terms should be included in the free-energy expression, since normal and excited atoms or molecules cannot be regarded as separate components. If they could be, then energy-rich molecules could possibly be separated from those of low energy by a suitable membrane; such a membrane would constitute a Maxwell demon and would consequently be contrary to the second law of thermodynamics.

one of which may be illustrated by means of Fig. 76. When the reacting system on the lower surface, *i.e.*, A_1 , reaches the activated state A_1^\ddagger , there is a probability of crossing (*cf.* page 148). The reacting molecules that pass to the upper surface

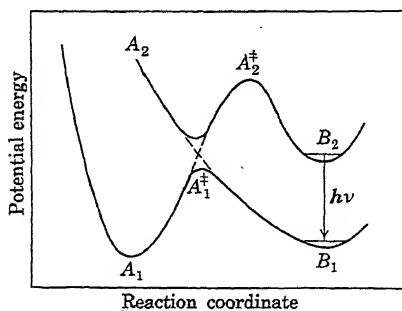


FIG. 76.—Chemiluminescence involving crossing of potential-energy surfaces.

in this manner and finally reach B_2 can return to the state B_1 , representing the reaction products in their lowest energy state, by emitting radiation of frequency ν as shown. Another possi-

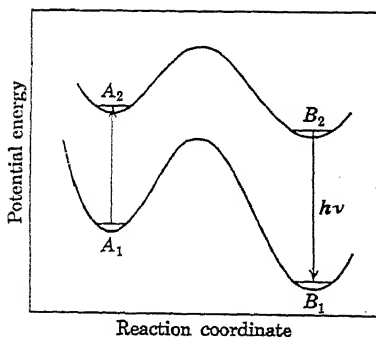


FIG. 77.—Chemiluminescence resulting from absorption of radiation in initial state.

bility that may be considered is that the transition from the lower to the upper surface occurs as the result of the absorption of suitable radiation in the initial state, *i.e.*, from A_1 to A_2 in Fig. 77. The system A_2 then undergoes reaction to form B_2 , and this returns to the lower state B_1 with the emission of radiation.

The maximum photon yield in a chemiluminescent reaction can be calculated by means of the results obtained above concerning radiationless transitions. The conclusion may be generalized in the form

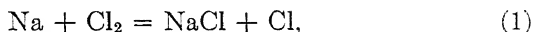
$$\frac{N_1}{N} \leq \frac{\Delta F}{E},$$

where N_1/N gives the photon, or fractional light, yield, *i.e.*, the fraction of the excited molecules that emit light, ΔF is the decrease of free energy in the chemiluminescent reaction, and E

is the energy of the quanta that are emitted. If ΔF is greater than E , it is clear that there is no restriction in the photon yield in the reaction. It is apparent from this discussion that it is possible for an endothermic reaction to be chemiluminescent, provided that it is accompanied by a decrease of free energy; the maximum light yield is determined by the relative magnitude of this quantity and the quantum of emitted radiation. How nearly the maximum efficiency is approached is determined by the reaction mechanism.

Alkali Metal-Halogen Reactions.—A particularly interesting group of chemiluminescent reactions, involving an alkali metal, generally sodium, and a halogen, or certain halides, has been studied by M. Polanyi and his collaborators.² These reactions fall into three general classes involving alkali metal vapor and (1) the halogen itself, (2) an inorganic halide or (3) an organic halide. In the first two classes the reactions are always accompanied by luminescence, but with the third the emitted radiation is appreciable only when the halide contains more than one halogen atom. In all the chemiluminescent processes with sodium as the alkali metal, the light emitted has been found to correspond to the sodium-*D* line, indicating that one stage in the reaction is accompanied by the formation of excited sodium atoms. In falling back to their ground state, these atoms emit the characteristic radiation.

If the reaction between sodium and chlorine is taken as typical of class (1) the first step is apparently

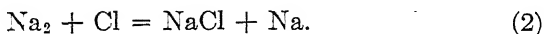


for the process occurs at about the rate predicted by the simple collision theory, it being assumed that the activation energy is zero. The observed rate is actually slightly greater than that calculated in this manner using ordinary collision radii, and the reason for this will be considered later (page 310). The occurrence of reaction (1) has been confirmed by chemical

² M. Polanyi, "Atomic Reactions," Williams and Norgate, London, 1932; H. Beutler and M. Polanyi, *Z. physik. Chem.*, **B**, 1, 3 (1928); S. von Bogdandy and M. Polanyi, *ibid.*, **B**, 1, 21 (1928); M. Polanyi and G. Schay, *ibid.*, **B**, 1, 30 (1928); H. Ootuka and G. Schay, *ibid.*, **B**, 1, 62, 68 (1928); H. Ootuka, *ibid.*, **B**, 7, 407 (1930); M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **35**, 178 (1939).

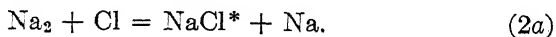
evidence for the presence of chlorine atoms in the reaction mixture. The heat evolved in the process is, however, only 40.7 kcal., and so it is incapable of exciting a sodium atom for which an energy of at least 48.3 kcal. is required.

The chlorine atoms produced in (1) can, theoretically, react with sodium atoms to yield sodium chloride; but, like other processes involving the combination of two atoms (*cf.* page 214), the reaction is exceedingly slow in the absence of a third body, as will be seen shortly. If the influence of the walls in this connection is made small, the chlorine atoms react with Na_2 molecules, thus:

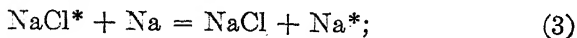


The evidence for this reaction is partly based on the fact that the intensity of the luminescence diminishes with increase of temperature, on account of the dissociation of the Na_2 molecules, and the heat of dissociation calculated from the results is in excellent agreement with the value obtained from spectroscopic data. Further, the chemiluminescence varies with the second power of the pressure of sodium vapor, consisting mainly of atoms, as is to be expected if reaction (2) occurs.

If the sodium chloride produced in this manner were in its lowest (ionic) state, the heat liberated would be about 75 kcal., which is sufficient to excite the sodium-*D* line. It would appear, at first sight, that the excited sodium atom is produced directly in reaction (2); but quenching experiments suggest that this is probably not the case. The effect of quenching substances is appreciably greater than would be expected if the process involved collisions between the added materials and sodium atoms. The suggestion has been made, therefore, that the energy produced in reaction (2) does not pass into the sodium atom but into the molecule of sodium chloride which becomes excited vibrationally (NaCl^*); thus:



The excited molecule is then supposed to transfer its additional vibrational energy, on collision with a sodium atom, into electronic energy of the latter, *i.e.*,



the excited sodium atom produced in this way then radiates its excess energy in the normal manner. Since the excited sodium chloride molecule exists for an appreciable time before passing its excess energy on to a sodium atom, the effect of quenching materials will be greater than if they had to remove the excess energy from the actual emitters, *i.e.*, the excited sodium atoms.

A careful consideration³ of the possible potential-energy surfaces for the sodium-chlorine system has shown, however, that there are three possible mechanisms for the reaction between Na_2 and Cl ; two of these lead directly to excited sodium atoms, and the third corresponds to the process mentioned above in which excited sodium chloride molecules are formed. The existence of the latter is sufficient to account for the results of quenching experiments, for these do not completely exclude the direct formation of excited sodium atoms by reaction (2). Before considering the various possible reactions between Na_2 and Cl , it is desirable to examine the interaction of sodium atoms first with chlorine atoms and then with chlorine molecules.

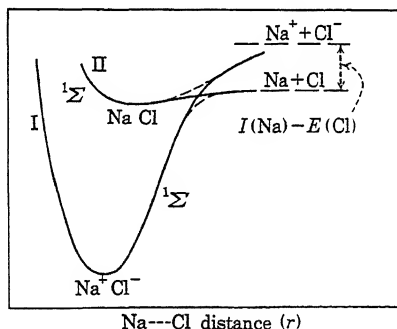


FIG. 78.—Potential-energy surfaces for atomic sodium-chlorine reactions. (Magee.)

Reaction between Alkali Metal and Halogen Atoms.—The normal ground state of sodium chloride consists of the ionic (polar) form Na^+Cl^- , but there is a possibility of the existence of a homopolar state NaCl with a higher potential energy. The variation with $\text{Na}-\text{Cl}$ distance of the potential energies of the two lowest states (1Σ) of sodium chloride is shown in Fig. 78, curve I being for Na^+-Cl^- and II for $\text{Na}-\text{Cl}$. The

³ J. L. Magee, *J. Chem. Phys.*, **8**, 687 (1940).

form of curve I is given, at least approximately, by the expression

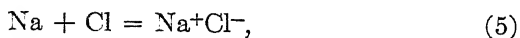
$$V = -\frac{\varepsilon^2}{r} + br^{-n}, \quad (4)$$

where r is the distance between the Na^+ and Cl^- ions, ε is the electronic charge, and b and n are constants. The first term, $-\varepsilon^2/r$, represents the coulombic attraction of the ions, and the second, br^{-n} , is the repulsion contribution (see page 143); the latter is negligible at distances appreciably greater than the equilibrium separation, and so the potential energy at the right-hand portion of curve I falls off inversely with the distance r . As a result, the attraction between ions extends to greater distances than for atoms, where the falling off is exponential, and the ionic curves do not approach their asymptotic values at large separations. Curve II is the potential-energy curve for the homopolar molecule of NaCl; there is evidently very little attraction between the sodium and chlorine atoms, and it is not certain whether or not the curve has actually a minimum corresponding to a stable homopolar state.

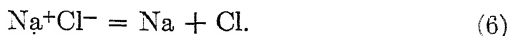
The distance between curves I and II at infinite value of r , *i.e.*, corresponding to complete dissociation into Na^+ and Cl^- in the former case and Na and Cl in the latter, is clearly equal to

$$I(\text{Na}) - E(\text{Cl}),$$

where $I(\text{Na})$ is the ionization potential of sodium atoms and $E(\text{Cl})$ is the electron affinity of atomic chlorine. For sodium chloride the values are 118.2 and 86.2 kcal., respectively, so that the distance between the curves I and II approaches 32.0 kcal. In the separated condition, the atoms are more stable than the ions, but when combined the ionic state is more stable than the homopolar form. The potential-energy curves must, therefore, cross, and they do so for a value of r of about 10.5 Å. (see Table XXXI, page 307). There is, of course, no actual crossing, as owing to resonance a separation takes place as indicated by the dotted lines in Fig. 78 (*cf.* page 136); there are thus two potential-energy surfaces, the lower being the one representing the reaction between sodium and chlorine atoms to form sodium chloride in its polar state, *viz.*,



or the reverse dissociation process



Apart from the partition functions and the frequency factor kT/h , the rates of these reactions are determined by the activation energy and by the transmission coefficient; these two factors will be considered in turn.

Activation Energy.—It has been seen (page 127) that in the association of two atoms to form a homopolar molecule the influence of rotation is important since the angular momentum acts as an additional potential and introduces a maximum in the potential-energy curve; this maximum represents the activated state for the particular rotational level. In the formation of a homopolar molecule, however, the angular momentum, which depends on $1/r^2$, cannot introduce a maximum in the attractive potential curve which varies as $1/r$; the influence of the former is merely to distort the latter. The position at which most restriction in the reaction under consideration occurs is at the crossing point of the curves for polar and homopolar states. The systems Na and Cl or Na^+Cl^- must reach this point before reaction can occur, and hence this may be regarded as the activated state; it is evident, therefore, that the activation energy for the association reaction (5) will be effectively zero, whereas that for the reverse process (6) will be the heat of dissociation of polar sodium chloride into sodium and chlorine atoms. According to the theory of absolute reaction rates, therefore, the specific reaction rate for the association process is

$$k = \kappa \frac{kT}{h} \cdot \frac{F_{\ddagger}}{F_{\text{Na}}F_{\text{Cl}}} \quad (7)$$

the F terms being the partition functions for unit volume. It is of interest to recall the result obtained on page 17 that for the combination of two atoms the absolute rate theory leads to the same expression as does the simple collision theory, apart from the transmission coefficient. It should be noted, however, that the correct numerical value for the reaction rate would be obtained only if the collision diameter were taken to be about 10.5 Å., *i.e.*, the atomic separation at the crossing point; the use of ordinary kinetic-theory diameters would give results that are too small (*cf.* page 310).

Transmission Coefficient.⁴—It is now necessary to consider the transmission coefficient κ , which it is convenient to examine from the standpoint of the dissociation reaction; the value for the association process must, of course, be the same (see page 287). Of the molecules that pass the crossing point from left to right, a certain fraction ρ will have come from the normal (polar) Na^+Cl^- molecules, the remainder coming from the homopolar state. Not all of this fraction will have originally started as Na^+Cl^- molecules; some will have originated in the dissociated state and will be passing from left to right because they were not stabilized in the molecular form. If σ is the fraction of those systems which originally came from the dissociated state and are stabilized, so that they do not recross from left to right, then

$$\kappa = \rho\sigma \quad (8)$$

gives the fraction of those molecules passing through the activated state, in the direction of dissociation, which originally started as Na^+Cl^- molecules. In the absence of a third body to remove the excess energy, the fraction is very small. The mean life of an oscillator of the type of Na^+Cl^- is known to be about 10^{-1} sec., estimated from the dipole moment, and hence it must oscillate roughly 10^{12} times during its life period. The probability that the molecule shall be stabilized, and hence the value of σ , is thus approximately 10^{-12} . It is evident that κ must be so small that the rate of reaction will be exceedingly slow in the absence of a third body. If the latter is present, however, it may be supposed that every collision between sodium and chlorine atoms leads to reaction, the product being either Na^+Cl^- or NaCl ; in these circumstances, σ is approximately unity, and ρ gives the value of the transmission coefficient.

The Zener-Landau equation (page 149) gives the probability χ that a molecule will make the *transition* from a lower to an upper state at the crossing point between two potential-energy surfaces. In the case under consideration, ρ is equivalent to the probability of the system *remaining* on the lower potential-energy surface, so that it is equal to $1 - \chi$, thus,

$$\rho = 1 - e^{-4\pi^2\epsilon^2/hv|s_i - s_f|}, \quad (9)$$

⁴ Magee, Ref. 3.

where the symbols ϵ , v , s_i and s_f have the same significance as before (page 149). The interaction energy ϵ , arising from the resonance between initial and final states, may be expressed approximately as

$$\epsilon = \int M(1)X(2)\mathbf{H}X'(1)X'(2) d\tau \quad (10)$$

where $M(1)$ is the orbital of the valence electron on M, and $X(2)$ that of the valence electron on X; X' is the valence orbital when occupied by two electrons. The symbol \mathbf{H} represents the perturbation-energy operator, given by

$$\mathbf{H} = \frac{1}{r_{MX}} + \frac{1}{r_{12}} - \frac{1}{r_{M2}} - \frac{1}{r_{X1}}, \quad (11)$$

and hence involves the distances between electrons and nuclei. In order to evaluate ϵ at the crossing point, it is first necessary to have some indication of the value of r_{MX} at this point. In its vicinity, it is obviously reasonable to neglect the repulsion term in Eq. (4); further, since curve II (Fig. 78) is almost horizontal, the potential energy relative to the separated ions is approximately the same as at infinity, i.e., $I(\text{Na}) - E(\text{Cl})$. Hence, at the crossing point,

$$I(\text{Na}) - E(\text{Cl}) \approx -\frac{e^2}{r_c} \quad (12)$$

$$\therefore r_c = -\frac{e^2}{I(\text{Na}) - E(\text{Cl})}, \quad (13)$$

where r_c represents the distance between the nuclei of sodium and chlorine at the crossing point. A similar equation is, of course, applicable to all the other alkali halides, and the values of r_c recorded in Table XXXI have been calculated from the known ionization potentials of the alkali metals and the electron affinities of the halogens.

TABLE XXXI.—INTERNUCLEAR DISTANCES AT CROSSING POINTS

	Li, Å	Na, Å	K, Å	Rb, Å	Cs, Å
F	11.7	14.6	76.5	495	*
Cl	8.9	10.5	25.0	35.2	120
Br	7.9	9.0	18.4	22.9	42.3
I	6.7	7.6	13.1	15.7	22.2

* No crossing.

These figures give the effective collision diameters for the reactions between the various alkali metal and halogen atoms; the values are seen to be greatly in excess of the normal atomic diameters, and it is apparent that, apart from the inability to estimate the transmission coefficient, simple collision theory would give results for the reaction rate which are seriously in error.

Utilizing the data in Table XXXI, J. L. Magee⁵ has made an approximate evaluation of the integral of Eq. (10), assuming 1s-orbitals, and has obtained the results given in Table XXXII for the values of the resonance energy between ionic and homopolar states at the crossing point; very large values are indicated by "v.l.," and very small ones by "v.s."

TABLE XXXII.—RESONANCE ENERGY AT CROSSING POINTS
(cal. per mole)

	Li	Na	K	Rb	Cs
F	12	4	10^{-24}	v.s.	...
Cl	228	219	10^{-3}	v.s.	v.s.
Br	v.l.	v.l.	10	1	v.s.
I	v.l.	v.l.	287	170	17

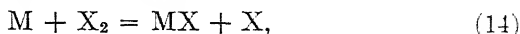
According to Eq. (9), ρ becomes larger as ϵ increases, and in fact ρ approximates to unity when ϵ becomes equal to kT . At 500°K , kT is about 250 cal. per mole, and ρ for sodium chloride ($\epsilon = 219$ cal.) is calculated as 0.93; for lithium fluoride, however, when ϵ is 12 cal., ρ is only 0.008. It will be seen by comparing Tables XXXI and XXXII that, in general, a large value of the nuclear separation at the crossing point will mean a small transmission coefficient. If r_c is small, however, there will be no restriction at the crossing point.

Since the rates of the alkali metal-halogen atomic reactions in the absence of a third body have little practical interest, the actual results will not be calculated. Sufficient information has now been obtained, however, to consider other aspects of the alkali metal-halogen reactions.

Reaction between Alkali Metal Atoms and Halogen Molecules.—The first step in the reaction between alkali metal vapor

⁵ Magee, Ref. 3.

and halogen, *i.e.*, reaction (1) (page 301), or in its general form



will now be examined. The reaction is very similar to that between M and X , the additional X atom having only a relatively small influence. The chief effect of the additional atom is to alter the value of r_c , the internuclear separation at the crossing point; this arises from the difference in the electron affinities between X and X_2 . The value for the latter will be less than for the former; and hence, as will be evident from Fig. 78, the separation between the atomic and ionic surfaces at high values of r will be increased. It follows, therefore, from Fig. 78 and from Eq. (13), that r_c will be increased. The electron affinity of the X_2 molecule may be regarded as less than that of the atom X by an amount equivalent to the binding effect of the additional valence electron; the latter quantity is equivalent to one-half the bond energy, or heat of dissociation, of the molecule X_2 , so that

$$E(X_2) \approx E(X) - \frac{1}{2}D(X_2), \quad (15)$$

where $D(X_2)$ is the heat of dissociation of the halogen molecule. By use of this approximation the value of r_c for the system $Na + Cl_2$ is found to be 5.5 Å. It is clear from what has been already said in connection with the $M + X$ reaction that for such a small value of r_c there will be no restriction at the crossing point and ρ may be taken as unity. Further, in the reaction (14) under consideration, σ will also approach unity, since a third body, the additional chlorine atom, will presumably act as a stabilizer by assisting in the removal of the excess energy. It follows, therefore, that the transmission coefficient κ can be taken as unity, and the specific reaction rate will be given by the expression

$$k = \frac{kT}{h} \cdot \frac{\frac{(2\pi m_+ kT)^{3/2}}{h^3} \cdot \frac{8\pi^2(8\pi^3 ABC)^{1/2} (kT)^{3/2}}{h^3} \prod^2 (1 - e^{-h\nu_+ / kT})^{-1}}{\frac{(2\pi m_M kT)^{3/2}}{h^3} \cdot \frac{(2\pi m_{X_2} kT)^{3/2}}{h^3} \cdot \frac{8\pi^2 I_{X_2} kT}{h^2} \cdot (1 - e^{-h\nu_i / kT})^{-1}} \quad (16)$$

the activation energy being zero. Since the energy is approximately the same in activated and initial states, there is no

additional potential operative in the former case. The diatomic molecule X_2 accordingly retains its rotational and vibrational degrees of freedom in the activated state, so that it behaves virtually as a single atom. The partition functions are thus similar to those concerned in a reaction between two atoms, and Eq. (16) reduces to one that is formally the same as that given by the simple collision theory* (see page 5), thus

$$k = r_c^2 \left[8\pi kT \left(\frac{m_M + m_{X_2}}{m_M m_{X_2}} \right) \right]^{1/2}, \quad (17)$$

although r_c has here the significance of the internuclear separation at the point where the two potential-energy surfaces cross. Equation (17) has been used, together with the values of r_c obtained in the manner described above, to calculate the specific rates of the reactions between Na and Cl_2 and between Na and I_2 . The results in Table XXXIII, which are in cc. mole⁻¹ sec.⁻¹, are seen to be in excellent agreement with the observed rates.

TABLE XXXIII.—CALCULATED AND OBSERVED SPECIFIC RATES OF $M + X_2$ REACTION

Reaction	Calc.	Obs.
Na + Cl_2	4.5×10^{14}	4.1×10^{14}
Na + I_2	6.0×10^{14}	6.1×10^{14}

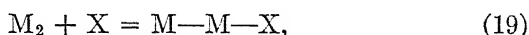
Since the values of r_c employed in Eq. (17) are at least twice as large as the corresponding figures for the mean diameters employed in the kinetic-theory equation for the collision number, the rates calculated here are about four times those given by the simple collision theory and are closer to the experimental results.

Reaction between Alkali Metal Molecule and Halogen Atom.
The reaction

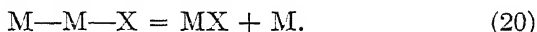


* As a consequence of the absence of an additional potential in the activated complex, one of the rotational degrees of freedom in the initial state is equivalent to a vibrational degree in the activated state; the vibrational terms, therefore, cancel. The rotational contribution of X_2 in the initial state cancels one in the activated state, thus leaving the contribution of two degrees of rotational freedom in the numerator.

is much more complicated than the one discussed in the previous section, on account of the fact that the excited states are so relatively low that they cannot be neglected. For convenience of representation of the potential-energy surfaces, the reaction may be considered as taking place in two stages, the first being the formation of the complex $M-M-X$, *viz.*,



and the second its decomposition, thus



First Stage.—The potential-energy surfaces for the first stage are shown in Fig. 79 for a linear approach of X to M_2 ; the

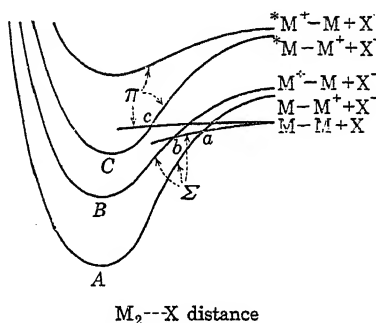


FIG. 79.—Potential-energy surfaces for the linear M_2-X system; M is an alkali metal and X is a halogen. (*Magee*.)

abscissae give the distance from X to the mid-point of M_2 . For the system consisting of an atom of X and a molecule of M_2 , the potential-energy curve is relatively flat, like II in Fig. 78.* There is here, however, a possibility of splitting into two levels, as shown on Fig. 79, *viz.*, Σ and Π , the latter having a slightly higher energy at the shorter M_2-X distances. Corresponding to curve I for M^+-X^- in Fig. 78, there are here two potential-energy curves, one for $M-M^+-X^-$, *i.e.*, when the M atom nearest to X^- is ionized, and one for M^+-M-X^- when the further atom is ionized. These two curves must approach each other for large M_2-X distances, but for small separations the

* To avoid complicating the diagram the curves for $M-M+X$ are discontinued beyond the crossing points.

one for $M-M^+-X^-$ will clearly have the lower potential energy, as depicted in Fig. 79; neither $M-M^+-X^-$ nor M^+-M-X^- is excited, and so both are in Σ states. It is now necessary to turn to the excited states, *viz.*, $*M-M^+-X^-$ and $*M^+-M-X^-$; these exist in both Σ and doubly degenerate Π states, but the potential-energy curves are otherwise exactly analogous to those just considered. To avoid complexity in the diagram, only those for the Π states are shown, the corresponding Σ curves being just below. All the curves approach each other for large M_2-X distances, but at short distances the ones for $*M-M^+-X^-$ will be the lower.

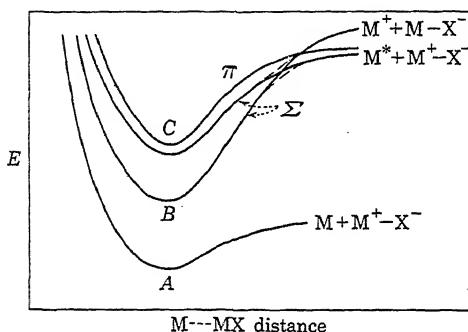


Fig. 80.—Potential-energy surfaces for the linear $M-MX$ system. (Magee.)

When a normal atom of X approaches a normal molecule of M_2 , the potential-energy curve is seen to cross that for $M-M^+-X^-$ at a ; since both curves represent Σ states, interaction is possible, with the result that reaction will proceed to the formation of the complex $M-M^+-X^-$ at the point A . If, however, there is a restriction at a , some of the molecules will proceed to b , when a crossing will take place to the curve for M^+-M-X^- , with the result that the complex M^+-M-X^- will be formed at B .

The Π (upper) surface for $M-M-X$ cannot interact with the two lower (Σ) states, because of symmetry restrictions; but a crossing is possible to the Π surface for $*M-M^+-X^-$ at c ; the complex $*M-M^+-X^-$ is thus formed at C .

Second Stage.—It is now necessary to consider the second stage of the reaction, *viz.*, the decomposition of $M-M-X$; the appropriate potential-energy curves, with the $M-(MX)$ distances as abscissae are shown in Fig. 80. The minima of the

curves in this figure are the same as the analogous ones in Fig. 79, and the right-hand asymptotes differ by the corresponding heats of reaction. The lowest curve, as is to be expected, is for the dissociation of $M-M^+-X^-$ (at *A*) into *M* and M^+-X^- . The complex M^+-M-X^- (at *B*) will dissociate into M^+ and $M-X^-$, and this will obviously be expected to have a relatively high energy, as shown. The right-hand side of the potential-energy curve, for which $^*M-M^+-X^-$ is the stable form (at *C*), represents $M^* + M^+-X^-$; and this will be above the lowest curve by an amount equivalent to the excitation energy of *M*. Since there are Π and Σ states for the system $^*M-M^+-X^-$, as mentioned above, although the Π curve only is shown in Fig. 79, there will be corresponding Σ and Π curves for the system $^*M-M^+-X^-$, and both are depicted in Fig. 80, that for the Σ state being the lower. It will be seen that the curve for M^+-M-X^- intersects the Σ curve for $^*M-M^+-X^-$, and since both represent Σ states there will be interaction with the formation of distinct upper and lower surfaces as shown by the dotted lines in Fig. 80. It follows, therefore, that the decomposition of M^+-M-X^- from *B* will result largely in the production of M^* and M^+-X^- , *i.e.*, excited *M* and *MX* in its normal (ionic) state. The same products are obtained from the complex $M^*-M^+-X^-$ in the Π state; the curve does not intersect with any other Π curve, and so there is direct decomposition from the equilibrium state at *C* to yield M^* and M^+-X^- , as seen in Fig. 80.

In reviewing the foregoing discussion, it is clear that a normal molecule of M_2 and a normal atom of *X* can react on three potential-energy surfaces: one, via the complex *A*, will lead to *M* and M^+X^- in their electronic ground states, the heat of reaction presumably passing into thermal motion of the molecule M^+X^- . This corresponds to the mechanism of Polanyi *et al.*, referred to previously (page 302). The other two modes of reaction via the complexes *B* and *C*, respectively, lead directly to excited *M* atoms; and hence it appears that part of the luminescence observed in the alkali metal-halogen reactions is due to the emission of radiation by excited alkali metal atoms produced *directly* in the chemical reaction. It will be seen shortly that owing to the lack of restriction at the crossing point *a* (Fig. 79) most of the reaction on the Σ surface of $M-M-X$ goes through *A* and leads to normal *M* and vibrationally excited M^+-X^- ;

hence, the process involving B does not occur to any great extent, but that through C is nevertheless of considerable importance.

Reaction through A.—As seen above, in connection with the $M + X$ reaction, the restriction at the crossing point depends to a large extent on r_c which, in turn, will be determined by $I(M_2) - E(X)$, as seen from Eq. (13). The value of r_c will be smaller than that for the simple reaction $M + X$ owing to the large ionization potential of M_2 as compared with that of M . Approximate calculations show that for reactions involving lithium and sodium molecules, at least, r_c is sufficiently small for ρ to be taken as unity; for potassium, rubidium and cesium, however, there may be an appreciable restriction to crossing at a .

Owing to the lack of restriction at a for reactions with sodium, the crossing at b (Fig. 79), to attain the system at B , can be neglected, and so it is necessary to consider only reactions via A and C . The Π state, as already mentioned, is actually doubly degenerate, and hence reaction through C must be weighted twice with respect to that through A ; this introduces factors of $\frac{2}{3}$ and $\frac{1}{3}$, respectively, in the equations based on the theory of absolute reaction rates, and on the assumption that the activation energy of the reaction is zero, as is probable from the position of the crossing point a , the specific rate of the reaction through A is given by

$$k_A = \frac{1}{3} \cdot \frac{kT}{h} \cdot \frac{F_{\ddagger}}{F_{M_2} F_X}. \quad (21)$$

As in the case of the reaction between M and X_2 , this reduces to the same form as Eq. (17), except for the factor $\frac{1}{3}$ that is introduced. If r_c is taken as 8.2 \AA. , the value of k_A for the specific reaction $\text{Na}_2 + \text{Cl}$ has been calculated in this way to be

$$\begin{aligned} k_A &= \frac{1}{3}(9.25 \times 10^{14}) \\ &= 3.08 \times 10^{14} \text{ cc. mole}^{-1} \text{ sec.}^{-1} \end{aligned} \quad (22)$$

Reaction through C.—The activated state for this reaction may be taken as the point c (Fig. 79); and here again the activation energy is zero, and Eq. (17) will be applicable, with the introduction of $\frac{2}{3}$ as the weighting factor. The distance r_c at the crossing point is calculated from $I(M_2^*) - E(X)$; for the reaction between Na_2 and Cl , this is estimated to be 4.7 \AA. , which is

sufficiently small for there to be no restriction at the crossing point (*i.e.*, $\rho \approx 1$). If this value of r_c is used, it is found that the specific rate for the reaction through *C* is given by

$$\begin{aligned} k_C &= \frac{2}{3}(3.04 \times 10^{14}) \\ &= 2.03 \times 10^{14} \text{ cc. mole}^{-1} \text{ sec.}^{-1} \end{aligned} \quad (23)$$

Total Reaction. The total specific rate for the reaction on the two surfaces, one leading to normal and the other to excited sodium atoms, is thus

$$\begin{aligned} k &= k_A + k_C = 3.08 \times 10^{14} + 2.03 \times 10^{14} \\ &= 5.11 \times 10^{14} \text{ cc. mole}^{-1} \text{ sec.}^{-1}, \end{aligned}$$

which may be compared with the experimental value of 1.5×10^{14} . It will be noted that according to the discussion presented here somewhat more than one-quarter of the reaction between sodium molecules and chlorine atoms leads to the direct production of excited sodium atoms. Similar calculations have been made for the reactions of sodium molecules with bromine and iodine atoms, and the results are presented in Table XXXIV, together with those obtained by experiment.

TABLE XXXIV.—SPECIFIC RATES OF $M_2 + X$ REACTIONS

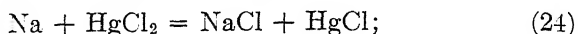
Reaction	Calc.	Obs.
$\text{Na}_2 + \text{Cl}$	5.1×10^{14}	1.5×10^{14}
$\text{Na}_2 + \text{Br}$	3.0×10^{14}	1.5×10^{14}
$\text{Na}_2 + \text{I}$	2.1×10^{14}	0.26×10^{14}

The discrepancies may be due to taking too large values for r_c in the reaction leading to unexcited atoms; but the agreement is, in any case, much better than that obtained by the simple collision theory. The collision diameters employed are considerably less than r_c , and the calculated rates are too low. It should be noted that the collision theory predicts increasing reaction rates in passing from chlorine to iodine, on account of the increasing atomic radii, and hence is contrary to experiment. No such discrepancy exists in the method of treatment described here.

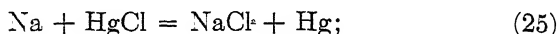
Attention may be called to the fact that the potential-energy curves in Figs. 79 and 80 and the calculations are based on a

linear M—M—X complex. The results have also been worked out for the approach of X along a line perpendicular to the line joining the two M nuclei, and the general conclusions are similar to those already given.

Reactions between Sodium Atoms and Inorganic Halides.⁶—Sodium vapor reacts with the vapors of mercuric chloride and bromide and of cadmium chloride with the production of luminescence. The primary process in the reaction with mercuric chloride, which may be regarded as typical, is

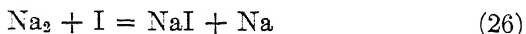


but the energy liberated, 25 kcal., is, as in the reaction with molecular chlorine, insufficient to excite the sodium-*D* line. The over-all rate of reaction is faster than collision theory predicts, indicating that there is in this case, also, no activation energy. The radical HgCl is formed in reaction (24); but this does not react with Na₂ molecules, as is the case with the chlorine atom in the sodium-halogen reaction, for the peculiar temperature and pressure effects, mentioned on page 302, are now absent. It appears, therefore, that the second stage in the reaction is



and if the NaCl were in its lowest state the energy evolved, 63.0 kcal., would be sufficient to excite a sodium atom. This excess energy is presumably carried by the sodium chloride as vibrational energy and is transferred to a sodium atom, which is thus excited electronically, as the result of a collision (*cf.* page 302).

The reactions between sodium atoms and the inorganic halides are distinguished by a low luminescence efficiency; as an example, the reaction between sodium and iodine may be contrasted with that between sodium and mercuric chloride. The reaction



has a heat of reaction only 1 kcal. in excess of the excitation energy of sodium, but the light yield is four times as great as for the reaction with mercuric chloride, in spite of the fact that

⁶ H. Ootuka and G. Schay, *Z. physik. Chem.*, **B**, **1**, 68 (1928); E. Horn, M. Polanyi and H. Sattler, *ibid.*, **B**, **17**, 220 (1932).

the excess energy in reaction (25) is 15 kcal. This problem will be considered in the next section.

Light Yields in Luminescent Reactions.⁷—It has been seen that in the sodium-chlorine reaction the ratio of the specific rate of the process leading to vibrationally excited sodium chloride and normal sodium atoms to that in which excited sodium atoms are produced directly is 3.08 to 2.03. Owing to the possibility of deactivation, however, only a fraction α of the excited sodium chloride molecules can pass their energy on to, and so excite, a sodium atom; the fractional light yield ϕ is, therefore, given by

$$\phi = \frac{3.08\alpha + 2.03}{5.11} \quad (27)$$

Because of the conservation of the translational and rotational energy of the complex as a whole, there are only three degrees of freedom into which the heat of reaction is allowed to go: (1) relative translation of the products, (2) rotation of the sodium chloride, and (3) vibration of the sodium chloride. The last may be assumed to be the most important. The probability that a system will have energy w in one degree of freedom when the total energy is W in s degrees of freedom, is given (see page 159) by

$$P(w) = \text{const.} \times (W - w)^{\frac{1}{2}s-1}. \quad (28)$$

The probability of the vibrational degree of freedom ($s = 2$) having energy between E' , the lowest energy that will excite luminescence, and E is, therefore,

$$\sim = \frac{\int_{E'}^E (W - w)^{\frac{1}{2}s-1} dw}{\int_0^E (W - w)^{\frac{1}{2}s-1} dw} = \frac{\int_{E'}^E dw}{\int_0^E dw} \quad (29)$$

$$\frac{E - E'}{E} \quad (30)$$

For the reaction between Na_2 and Cl the energy E available is 74 kcal.; and since the minimum amount E' necessary to excite a sodium atom is 48 kcal., it follows that

$$\alpha = \frac{74 - 48}{74} = 0.35. \quad (31)$$

⁷ Magee, Ref. 3.

Insertion of this value in Eq. (27) gives, for the fractional light yield, $\phi = 0.61$, which is lower than the experimental value 0.8. It may be pointed out that the calculations are inevitably approximate since Eqs. (29) and (30) are based on the assumption of random distribution, whereas in the processes being considered certain states are favored.

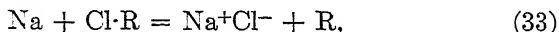
If the reaction occurs between the alkali metal and a halide, there is no possibility of direct excitation; hence, it follows from Eq. (27) that the fractional light yield ϕ will be equal to α . The result is that ϕ is lower than for the corresponding reaction in which the halogen itself is concerned. As seen above, E for reaction (25), involving mercuric chloride, is 63 kcal.; hence, it follows that

$$\phi = \alpha = \frac{63 - 48}{63} = 0.23. \quad (32)$$

The experimental value is actually lower, *viz.*, 0.1; but that calculated is less than would have been the case if there had been direct, in addition to indirect, excitation.

Much valuable information on the mechanism of the chemiluminescent reactions with alkali metal vapors could be obtained by careful quenching experiments. In particular, there should be a difference between reactions in which the halogen itself or a halide takes part. Further, owing to the restriction at the appropriate crossing point analogous to a in Fig. 79, the reactions between chlorine and rubidium and cesium vapors can presumably occur only by mechanisms involving direct excitation of the alkali metal; the quenching phenomena should thus differ markedly from those observed with lithium and sodium where indirect excitation is possible.

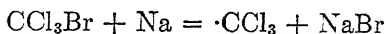
Reaction between Alkali Metals and Organic Halides.—Reactions of the type



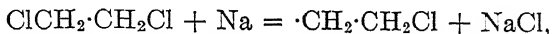
where R is an alkyl or aryl radical, are generally not accompanied by luminescence, for the energy produced is not sufficient to excite the alkali metal atom. If the organic halide contains two or more halogen atoms, however, luminescence is often observed;⁸ and this is attributed to the energy produced when

⁸ C. E. H. Bawn and W. J. Dunning, *Trans. Faraday Soc.*, **35**, 185 (1939); J. N. Haresnape, J. M. Stevels and E. Warhurst, *ibid.*, **36**, 465 (1940).

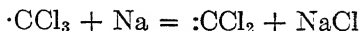
the second, or third, halogen atom is removed by the sodium. The removal of the first halogen results in the formation of a free radical, thus,



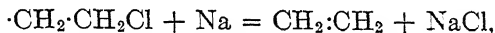
or



with the liberation of a small amount of energy; but in the next stage there is a considerable gain, resulting from the pairing of the two odd electrons, thus,



or



so that the excess energy may well be sufficient to excite a sodium atom.

Although not always accompanied by luminescence, processes involving an alkali metal and an organic halide will be discussed here,⁹ since they are of the same general nature as the reactions already considered in this chapter. No activation energies for these reactions have been measured directly, but it has been inferred that they are not zero from the fact that the reactions occur more slowly than those in which halogens or inorganic halides take part. Approximate values have been obtained in a number of cases by assuming the simple collision theory to be applicable; the activation energies obtained in this manner for the reaction between sodium vapor and the vapors of methyl and phenyl chloride, bromide and iodide are given in Table XXXV.

TABLE XXXV.—“OBSERVED” ACTIVATION ENERGIES FOR REACTIONS WITH SODIUM

CH_3Cl	9.7 kcal.	CH_3Br	4.7 kcal.	CH_3I	~0 kcal.
$\text{C}_6\text{H}_5\text{Cl}$	10.2 kcal.	$\text{C}_6\text{H}_5\text{Br}$	4.6 kcal.	$\text{C}_6\text{H}_5\text{I}$	1.7 kcal.

An examination of the data for the number of classical collisions necessary for reaction, the so-called “collision yield,”

⁹ H. von Hartel, N. Meer and M. Polanyi, *Z. physik. Chem.*, **B**, **19**, 139 (1932); J. Heller and M. Polanyi, *ibid.*, **B**, **32**, 633 (1933); F. Fairbrother and E. Warhurst, *Trans. Faraday Soc.*, **31**, 987 (1935); J. L. Tuck and E. Warhurst, *ibid.*, **32**, 1501 (1936).

which is an approximate measure of the activation energy, in a large number of instances, shows that the rate of reaction is favored by:

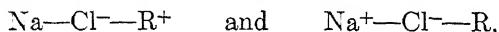
1. Increase in the atomic number of the halogen.
2. Increase in length and, particularly, branching of the hydrocarbon chain.
3. Introduction of negative groups into the alkyl radicals.
4. Introduction of a double bond in the 2-3 position.
5. Removal of a double bond from the 1-2 position.

There appears to be a parallelism between the reactivity of an alkyl chloride with sodium vapor and the atomic refraction of the halogen atom, as may be seen from the data in Table XXXVI.¹⁰

TABLE XXXVI.—ATOMIC REFRACTION AND REACTIVITY OF HALOGEN

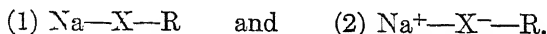
Halide.....	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄
Atomic refraction.....	6.19	6.33	6.47	6.61
Collision yield.....	7,100	760	50	5.5

Similar results have been obtained in other instances; and it appears that the greater the polarizability of the halogen atoms or, more probably, the greater the ionizability of the C—X bond, where X is a halogen atom, the more readily does the reaction with alkali metal vapor occur. The greater the ionizability of the bond, the greater will be the resonance in the activated state between the structures



and so the lower will be the activation energy, and hence the "collision yield," to which it is related. The results can thus be explained, at least qualitatively.

Calculation of Activation Energies.—Attempts have been made to calculate the activation energies for reactions between sodium vapor and alkyl and aryl halides, R·X, where X is the halogen, by using the method described on page 142.¹¹ The reaction is considered as a transition between the linear bond configurations represented by



¹⁰ Haresnape, Stevels and Warhurst, Ref. 8.

¹¹ R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, **31**, 1375 (1935); M. G. Evans and E. Warhurst, *ibid.*, **35**, 593 (1939).

The energy E_1 of state (1) for any linear configuration of the centers can be expressed in terms of the energy B_1 of the X—R bond and the repulsion energy R_1 arising from the repulsion forces between Na and X—R: thus,

$$E_1 = B_1 + R_1, \quad (34)$$

and, similarly, for state (2)

$$E_2 = B_2 + R_2. \quad (35)$$

It has been suggested that a sodium atom is able to approach a halogen atom, held by a homopolar bond to the radical R, up to the normal bonding distance without incurring any appreciable repulsion (*cf.* page 144);¹² if this is the case, R_1 can be neglected, and the problem is simplified because it is possible to represent the potential-energy surface in terms of one parameter, *viz.*, the X—R distance.

The method of constructing the surfaces corresponding to the configurations (1) and (2) follows closely the procedure described on page 142; the values of B_1 are obtained from the Morse equation for the C—X bond in the halide, derived from spectroscopic data. The bond energy B_2 is calculated from Eq. (56) or (57), Chap. III, and the repulsion energy R_2 is given by

$$R_2 = -\frac{\alpha\epsilon^2}{2r^4} + br^{-9}, \quad (36)$$

where the first term, involving the polarizability α of the organic radical, represents the attraction arising from the influence of the charged halide ion on the R group and the second term is the normal repulsive contribution, which may alternatively be represented by $be^{-\tau/r}$.

Having evaluated E_1 and E_2 for various values of r_1 , the X—R distance, the curves are adjusted relative to each other along the energy coordinate so as to give the correct value of the heat of reaction; the point of intersection is then assumed to give the energy of activation. The results obtained for methyl and phenyl halides are given in Table XXXVII; for those in column I the repulsion term br^{-9} was used in calculating R_2 , whereas for those in II the modified exponential form was employed. The

¹² M. G. Evans and M. Polanyi, *ibid.*, **34**, 11 (1938).

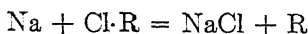
values in column III were obtained after making an allowance for the repulsion term R_1 (cf. page 143), which was neglected in the other calculations.

TABLE XXXVII.—CALCULATED AND "OBSERVED" ACTIVATION ENERGIES FOR REACTION BETWEEN Na AND R·X

R·X	Calc., kcal.			Obs., kcal.
	I	II	III	
CH ₃ Cl	16.2	17.7	15.0	9.7
CH ₃ Br	8.7	14.2	7.1	4.7
CH ₃ I	6.1	12.7	2.8	0
C ₆ H ₅ Cl	11.3	~16	10.2
C ₆ H ₅ Br	3.0	~16	4.6
C ₆ H ₅ I	0.7	~16	1.7

The general agreement between calculated and observed results is only fair; and in view of the uncertainty as to the form of the repulsion curve R_2 , which has a marked effect on the calculated activation energies (compare columns I and II), the results cannot be regarded as very significant. It must be remembered, too, that no allowance has been made for resonance at the crossing point of the E_1 and E_2 surfaces, representing the activated state, and for this reason the calculated activation energies must be in error. In making a comparison between observed and calculated values, it must be borne in mind that the former are derived on the basis of the assumption that the simple collision theory is applicable. In view of the results obtained with the reactions between sodium atoms and halogen molecules, this procedure may be open to question; but, as will be seen shortly, the errors arising in this way are probably not large.

It is reasonably certain, in any case, that reactions of the type



have an appreciable activation energy, whereas those involving a molecule of chlorine or of an inorganic halide, *e.g.*, HgCl₂, have none. The explanation of this behavior may lie in the difference between the electron affinities of chlorine and mercuric chloride

on the one hand and of the organic halides on the other. The values for the latter group are probably much smaller than for the former, so that $I(\text{Na}) - E(\text{Cl}_2)$ is considerably less than $I(\text{Na}) - E(\text{R}\cdot\text{Cl})$; the result of this may be seen in the potential-energy curves in Fig. 81. Apart from any possible change in shape, the curve for $\text{Na}-\text{Cl}-\text{R}$ is lower than that for $\text{Na}-\text{Cl}-\text{Cl}$; hence, the rising (repulsion) portion is reached before the crossing point representing the activated state. There is consequently a small, but definite, activation energy. It should be noted that r_c for $\text{Na}-\text{X}-\text{R}$ is less than for $\text{Na}-\text{X}-\text{X}$; the result of this is twofold. In the first place, there will be no appreciable restriction to crossing, so that κ is almost unity;

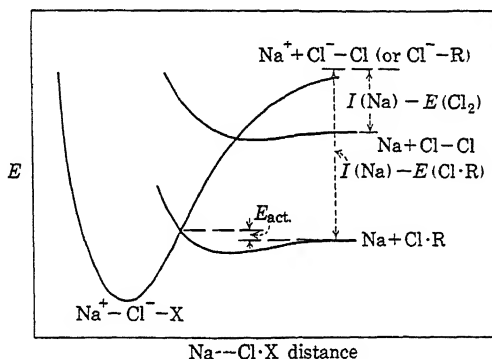


FIG. 81.—Potential-energy surfaces for the linear $\text{Na}-\text{Cl}\cdot\text{X}$ system. (Magee.)

in the second place, the effective diameter to be used in the kinetic-theory expression for the collision number [Eq. (17)] will not differ very greatly from the normal mean diameter. It is probable, therefore, that the simple collision theory will be approximately applicable to reactions involving an alkali metal atom and a simple alkyl, or aryl, halide.

CIS-TRANS ISOMERIZATION REACTIONS

Two Types of Reaction.—The experimental results¹³ on the cis-trans isomerization reactions of ethylenic derivatives, which involve a rotation of 180 deg. about the double bond, show that

¹³ G. B. Kistiakowsky *et al.*, *Z. physik. Chem.*, A, **152**, 369 (1931); *J. Am. Chem. Soc.*, **54**, 2208 (1932); **56**, 638 (1934); **57**, 269 (1936); **58**, 766, 2428 (1936); B. Tamamushi and H. Akiyama, *Z. Elektrochem.*, **43**, 156 (1937); **45**, 72 (1939); *Bull. Chem. Soc. Japan*, **12**, 382 (1937).

these processes can be divided into two classes. It can be seen from the data in Table XXXVIII that in one group of reactions the specific reaction rates are given, approximately, by the expression

$$k \approx 10^4 e^{-25,000/RT} \text{ sec.}^{-1},$$

whereas in the other

$$k \approx 10^{11} e^{-45,000/RT} \text{ sec.}^{-1}$$

In other words, one group is characterized by a low frequency factor A and a low energy of activation $E_{\text{exp.}}$ in the equation $k = A e^{-E_{\text{exp.}}/RT}$, whereas in the other these quantities are high; the actual specific rates, however, do not differ very greatly at the experimental temperatures, about 300°C.

TABLE XXXVIII.—KINETICS OF CIS-TRANS ISOMERIZATION REACTIONS

Reactant	Temp., °c.	Press., mm.	A	$E_{\text{exp.}}$, kcal.
Maleic acid (<i>l</i>).....	140 to 150	1.7×10^4	15.8
Dimethyl maleic ester (<i>g</i>)...	270 to 380	45 to 530	1.3×10^5	26.5
Dimethyl citraconate (<i>g</i>)...	280 to 360	30 to 500	10^5	25.0
Butene-2 (<i>g</i>).....	390 to 420	100 to 1,440	2(?)	18.0 (?)
Methyl cinnamate (<i>g</i>).....	290 to 387	5 to 500	3.5×10^{10}	41.6
β -Cyanostyrene.....	303 to 378	20 to 450	4×10^{11}	46.0
Stilbene (<i>g</i>).....	280 to 338	4 to 400	6×10^{12}	42.8
Stilbene (<i>l</i>).....	214 to 223	2.7×10^{10}	36.7
Monochlorostilbene (<i>l</i>).....	226 to 246	1.4×10^{11}	37.0
Dichlorostilbene (<i>l</i>).....	175 to 196	9.9×10^{10}	34.1

The reactions in both groups are kinetically of the first order, and for such reactions the frequency factor A is normally about 10^{13} (see page 296). In view of the large discrepancy between this figure and that found, *viz.*, 10^4 , for one group of cis-trans isomerizations, it is highly probable that the reactions in this group are nonadiabatic in character. If the isomeric change involves a crossing from one potential surface to another, it is possible, if the interaction between the two states is small, for the transmission coefficient to be so low as to account for the difference between the observed frequency factor and that to be expected for a normal unimolecular reaction.

Singlet and Triplet States of Ethylene.—The ethylene molecule has a singlet ground state; and since a rotation of 180 deg. about the double bond leads to an equivalent structure, this must also be a singlet state. The variation of potential energy of these two states of ethylene with the angle θ of rotation about the double bond may thus be represented schematically by two curves IA and IB of the parabolic type shown in Fig. 82. The lowest excited state of the ethylene molecule is presumably a triplet¹⁴; and there is reason for believing that in this state the energy depends very little on rotation, especially if θ does not differ considerably from 90 deg. The potential energy of the triplet state is thus represented, approximately, by a horizontal line III in Fig. 82; and there is reason for believing that its position is well below the crossing point of curves IA and IB. The existence of a low triplet state for ethylene is not surprising when it is remembered that this substance is isoelectronic with the oxygen molecule, and the latter is actually a triplet in its ground state.

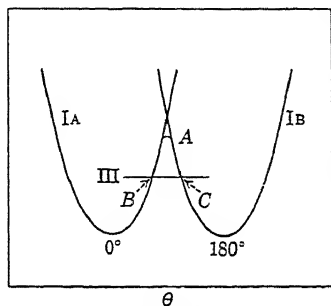


FIG. 82.—Potential-energy curves for rotation of ethylene about the double bond.

Reaction Mechanism.¹⁵—If the potential curves in Fig. 82 may be supposed to apply generally to ethylene derivatives, then curves IA and IB may be regarded as those of cis- and trans-forms, respectively. The isomerization process thus involves the transfer of the system from one curve to the other, and this can clearly take place in two ways. In the first method the system moves from IA to IB without change of multiplicity; *i.e.*, the molecule remains in a singlet state throughout. If it were not for resonance, the activated state would be at the crossing point of the two curves; but the considerable interaction between the two equivalent structures results in a marked lowering of the potential energy, so that the actual reaction path is shown by the dotted line, the point A being the activated state. The alternative method whereby the cis-trans isomeriza-

¹⁴ R. S. Mulliken, *Phys. Rev.*, **41**, 751 (1932).

¹⁵ J. L. Magee, W. Shand and H. Eyring, *J. Am. Chem. Soc.*, **63**, 677 (1941).

tion may occur is for the system to undergo an electronic transition from the singlet to the triplet state at *B* and then back to the singlet state at *C*. In view of the small interaction between singlet and triplet states the probability of transfer is small, and hence the reaction will have a very low transmission coefficient with the result that the frequency factor will be small. It can be seen, in general, therefore, that it is reasonable to suggest that the former mechanism, through the activated state *A*, represents that with the high activation energy and high frequency factor, whereas the alternative mechanism, through *B* and *C*, is that with low activation energy and frequency factor.

By taking the torsional frequency ν_θ of ethylene to be 825 cm.^{-1} and using the known dimensions of the molecule, the corresponding force constant f_θ can be calculated by means of the formula

$$\nu_\theta = \frac{1}{2\pi} \sqrt{\frac{f_\theta}{I_r}}, \quad (37)$$

where I_r is the reduced moment of inertia for rotation about the double bond. The result is 3.75×10^{12} dynes per radian; and on the assumption that the potential energy V is a parabolic function of the angle of rotation, thus,

$$V = \frac{1}{2} f_\theta \theta^2, \quad (38)$$

the potential-energy curves can be drawn. The crossing point of the curves *I_A* and *I_B* obtained in this manner is found to be at 63 kcal. per mole above the minima. If the resonance energy is about 20 kcal., as is not unreasonable in view of the similarity between the two interacting structures, the activation point should be at approximately 40 to 45 kcal. above the ground level. This is in satisfactory agreement with the experimental activation energies for one group of the isomerization reactions. The exact position of the potential-energy curve for the triplet state cannot be estimated readily, but it may be set at about 20 kcal. above the singlet minimum in accordance with the activation energies in the second group of reactions.

Reaction with Low Activation Energy.—In most reactions, there is a classical motion along the reaction path, or at least on one side of the activated state; a unimolecular decomposition, for example, leads from a quantized vibrational level to a con-

tinuum of translational levels. In the reactions under consideration, this is not the case because each of the three potential curves shown in Fig. 82 represents a series of well-quantized rotational-energy levels. By making the approximation that the energy levels for rotational motion about the activated state are very closely spaced, the reaction can be treated as classical. Since the quantization restricts the motion, the classical rate should be somewhat larger than would be obtained by introducing the appropriate restrictions.

For the reaction of low activation energy, the activated state will occur at either *B* or *C*; the passage at one of these will be rate-determining, and it is assumed that the point *B* is the critical one. The specific rate of the reaction can be written in the familiar form (page 190)

$$k = \kappa \frac{kT}{h} \cdot \frac{F_{\ddagger}}{F_i} e^{-E_0/RT}, \quad (39)$$

where F_i and F_{\ddagger} are the partition functions of initial and activated states, respectively; the latter corresponds to the partition function of a normal ethylene molecule with the exception that the degree of freedom of torsional vibration has been removed. If the properties of the activated molecule are identical with those of the normal molecule, with the exception of this torsional motion, the translational, vibrational and rotational contributions to the partition function cancel leaving only that due to the torsion; it follows, therefore, that Eq. (39) can be reduced to

$$k = \kappa \frac{kT}{h} (1 - e^{-h\nu_\theta/kT}) e^{-E_0/RT} \quad (40)$$

where ν_θ represents the torsional frequency of the normal molecule.

The Transmission Coefficient.—The transmission coefficient is the product of two factors: one (ρ) giving the probability for the transfer from the singlet to the triplet state at *B*, and the other (σ) correcting for the fact that a certain fraction of the reacting systems which pass the point *B* and make the transition will return to the initial state. The latter factor depends, in this case, on the ease with which the activation energy can be transferred to other molecules and so will depend on the pressure. If the product is not deactivated, it can clearly return to the initial state since it will have sufficient energy to do so.

At high pressures, it may be supposed that all systems passing the point *B* become deactivated, and so under these conditions σ is unity, and the transmission coefficient κ is equal to the ρ factor. As on page 306, ρ is the probability that the system will remain on the lower of the two potential-energy surfaces into which Ia and III split at the crossing point *B* (Fig. 82), so that it is given by Eq. (9). If the resonance energy is small, as it is for the processes under consideration, this becomes (*cf.* page 150)

$$\rho = \frac{4\pi^2\epsilon^2}{\hbar v |s_i - s_f|}. \quad (41)$$

Upon taking v as 10^{13} radians per sec. and $|s_i - s_f|$ as 40 kcal. per mole per radian, which are reasonable values, it follows that

$$\rho = 1.04 \times 10^{-6}\epsilon^2, \quad (42)$$

where ϵ is now expressed in calories per mole.

The connection between singlet and triplet states is due to spin-orbit interaction; its extent is small, values of less than 1 cal. having been calculated for ethylenic derivatives. It is seen, therefore, that ρ , which at relatively high pressures is equal to the transmission coefficient, is of the order of 10^{-7} . The value of the reciprocal of the torsional partition function, *i.e.*, $1 - e^{-\hbar\nu_\theta/kT}$, in Eq. (40) is somewhat less than unity; and since kT/\hbar is about 10^{13} , it follows that the frequency factor, which according to Eq. (40) is approximately equal to

$$\kappa \frac{kT}{\hbar} (1 - e^{-\hbar\nu_\theta/kT}),$$

will be about 10^5 to 10^6 for the isomerization reaction of low activation energy. Detailed calculations give 3.7×10^5 for the cis-trans change of dimethyl maleic ester and 2.5×10^5 for butene-2; the former figure is seen to be in good agreement with that obtained by experiment (Table XXXVIII), but for the latter there is still a considerable discrepancy.

An attempt has been made to introduce the quantum restrictions mentioned above on the basis of the quantum-theory postulate that electronic transition, *e.g.*, from singlet to triplet states, can occur only between energy levels that are in resonance, *i.e.*, levels that are almost exactly matched. It appears that in maleic ester the torsional levels are very closely spaced, and

so the behavior in this case is virtually classical; the frequency factor for the cis-trans isomerization is calculated as 1.9×10^4 , which is less, by about a factor of 10, than the value already derived. In butene-2, however, the energy levels along the reaction coordinate are probably widely spaced, and the frequency factor, introducing the quantum restrictions, is estimated to be 2.7×10^3 . This is an improvement on the result obtained by classical methods, but it still differs appreciably from the experimental value. It must be pointed out that the frequency factor for the isomerization of butene-2 is much smaller than for the other substances studied so far, and so it may be exceptional in certain respects.

Low-pressure Reaction.—At fairly low pressures the transmission factor σ is of importance and must be considered; the value of σ is equal to the ratio of the rate at which the molecules become deactivated, after passing the point *B*, to the total rate of all the reactions, including returning to the initial state, that the molecules are able to undergo. Deactivation can occur as a result of collision with other molecules or by the transfer of energy to other, generally vibrational, degrees of freedom in the activated molecule. If ν_c is the collision frequency for all the molecules present in the system, the frequency of collisions between activated and normal molecules will be $\nu_c e^{-E_0/RT}$, since a fraction $e^{-E_0/RT}$ of the molecules are activated. The probability of deactivation in a collision is α_c , and so the rate of deactivation by collision is given by $\alpha_c \nu_c e^{-E_0/RT}$. Similarly, if ν_i is the frequency with which the possibility arises for transfer of energy to the *i*th vibration and α_i is the corresponding probability of deactivation, the rate of transfer of energy for the activated molecules is given by $\alpha_i \nu_i e^{-E_0/RT}$. Since the energy is still in the molecule, however, it can return to the original, *i.e.*, torsional, degree of freedom after a time τ_i for the *i*th vibration; and hence it is not certain that the transfer of energy will result in deactivation. The energy must ultimately be removed by collision, and therefore the rate of deactivation by transfer of energy to other degrees of freedom, represented by the symbol ω , is given by

$$\omega = \sum_{i=1}^n \alpha_i \nu_i e^{-E_0/RT} \frac{\alpha_c \nu_c e^{-E_0/RT}}{\frac{1}{\tau_i} + \alpha_c \nu_c e^{-E_0/RT}}, \quad (43)$$

where m is the number of vibrational modes into which the activation energy can go. In addition to the transfer of energy by collision and by internal rearrangement, all the molecules that have passed the activation point have the possibility of returning; the total rate at which this may occur is equal to the reaction rate, *i.e.*, $A e^{-E/RT}$, where A is the frequency factor, *i.e.*, about 10^5 . The sum of the rates of all the reactions that an activated molecule can undergo is thus

$$(A + \alpha_c \nu_c + \sum \alpha_i \nu_i) e^{-E_0/RT};$$

and hence, according to the definition given above,

$$\alpha_c \nu_c + \omega e^{-E_0/RT} \quad (44)$$

$$A + \alpha_c \nu_c + \sum_1^m \alpha_i \nu_i$$

If it is assumed that all the $\alpha_i \nu_i$ terms are zero, *i.e.*, that there is almost no transfer of energy from one internal degree of freedom to another, Eq. (44) reduces to

$$\sigma = \frac{\alpha_c \nu_c}{A + \alpha_c \nu_c}, \quad (45)$$

which is of the form found experimentally. In the isomerization of dimethyl maleic ester the rate becomes pressure-dependent at about 1 atm.; the collision frequency ν_c is then of the order of 10^9 , and so it follows, since A is approximately 10^5 , that α_c must be about 10^{-4} . The experimental data for dimethyl maleic ester give a value of 5×10^{-5} for α_c , so that the correspondence with theory is satisfactory. For butene-2, however, the agreement is poor; but this may be due to the neglect of quantization which is of greater significance with this substance than with the maleic ester.

Reaction of High Activation Energy.—As in the case already considered, the activated state will differ from the initial state by the torsional vibration only; and hence the specific rate is given by an equation of the same form as (40), the main differences lying in the activation energy and the value of the transmission coefficient. If the latter is taken as unity, it is evident that the frequency factor will be about 10^{13} , which is somewhat larger than that actually found by experiment. The difference

is probably due to the transmission coefficient being less than unity, as will be evident shortly. The value of κ in this case is also given by Eq. (44), but it is probable here that the $\alpha_i\nu_i$ terms are much larger than for the low-activation-energy reaction. A possible reason for this is that in the activated state the angle of rotation θ is now 90 deg., and the torsional motion is no longer to be regarded as a vibration, but as a rotation which can interact strongly with the other vibrations of the molecule. The probability of the transfer of energy to vibrational modes within the molecule will thus be quite appreciable. It should be mentioned that the high-activation-energy reactions are apparently not pressure-dependent, and this can be readily explained if the $\alpha_i\nu_i$ terms in Eq. (44) play the dominant part. In other words, for this type of reaction, most of the molecules after passing through the activated state are deactivated by the rearrangement of energy within the molecule. In view of the fact that it is not possible to make estimates of the α_i and ν_i terms the value of κ cannot be calculated, but it is reasonably safe to say that it will be somewhat less than unity.

Choice of Reaction Path.—In view of the fact that two alternative reaction paths are available for the cis-trans isomerization of ethylene derivatives, a question arises concerning the conditions that determine the particular path a given substance will take. It appears from Table XXXVIII that compounds containing benzene rings prefer the high-activation-energy path; a possible explanation of this fact is that when the double bond becomes a single bond, *i.e.*, at the activated state, in the singlet level the energy of the molecule depends on the ability of the two electrons thus made available to form other bonds. In molecules with phenyl groups attached to the ethylenic carbon atoms there is ample opportunity for resonance, and so the singlet activated state has a lower potential energy than would be the case for molecules, such as butene-2 and maleic ester, where similar resonance cannot take place. The resulting decrease in the activation energy for the upper path for benzene derivatives makes this route the more favorable of the two alternatives. An interesting possibility, which does not appear to have been observed, would be a cis-trans isomerization in which the reaction path changed as the experimental conditions were altered.

Tunneling in Rotation about Double Bonds.—In view of the fact that the ammonia molecule penetrates a narrow potential barrier as a result of quantum-mechanical leakage, or "tunneling," at a frequency of about 10^{10} per second in an inversion type of reaction, it is necessary to consider whether the two different cis-trans isomerizations could be explained by leakage at different energy levels. For high levels the barrier is narrow (Fig. 82) and the frequency would be high, whereas at a lower level the tunneling frequency would be much lower. It is thus possible to account qualitatively for the two mechanisms observed, although it is not clear why there should not be a large number of such mechanisms.

The appropriate form of the rate equation for inversion by leakage through the barrier at the n th level of the torsional vibrator is analogous to Eq. (40), thus,

$$k_n = \frac{\Delta_n}{h} (1 - e^{-h\nu/kT}) e^{-(n+\frac{1}{2})h\nu/kT}, \quad (46)$$

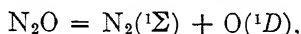
where Δ_n/h represents the tunneling frequency at the n th level and ν is the torsional vibration frequency; the quantity $(n + \frac{1}{2})h\nu$ is the vibrational energy, in excess of the minimum of the potential-energy curve, in the n th level. The quantity Δ_n/h can be derived by the method employed by D. M. Dennison and G. E. Uhlenbeck¹⁶ in connection with the ammonia problem, and hence k_n can be estimated. For ethylene, the energies of the tenth and twentieth levels are 25 and 48 kcal., respectively, which correspond approximately to the activation energies for the cis-trans-isomerization mechanisms; the corresponding frequency factors, as given by Eq. (46), are 7.2×10^3 and 5.2×10^{11} , which are in fair agreement with those obtained experimentally. It appears, therefore, that for ethylene the rate of tunneling is of the right order of magnitude to be of importance in isomerization reactions. With ethylenic derivatives, however, there is no such correlation between calculated and observed frequency factors. The large values of the reduced moments of inertia for the torsional vibration result in a much decreased rate of tunneling, and the frequency factors calculated are smaller, by many orders of magnitude, than those derived from the experimental

¹⁶ D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.*, **41**, 313 (1932); see also F. T. Wall and G. Glockler, *J. Chem. Phys.*, **5**, 314 (1937).

data. The possibility of interpreting the cis-trans isomerization results in terms of quantum-mechanical leakage must thus be ruled out.

THERMAL DECOMPOSITION OF NITROUS OXIDE

Potential-energy Surface.—The dissociation of nitrous oxide into a molecule of nitrogen and an atom of oxygen is a reaction that is accompanied by an electronic transition. The normal state of nitrous oxide is ${}^1\Sigma$, whereas that of a nitrogen molecule is ${}^1\Sigma$ and of atomic oxygen 3P ; these products can be obtained only if there is a change in the electronic state of the oxygen, for the decomposition of ${}^1\Sigma$ nitrous oxide would otherwise lead to an oxygen atom in the 1D state. The problem of the construction of the potential-energy surface for this reaction falls into two parts: (1) that for the dissociation



and (2) for the system $\text{N}_2({}^1\Sigma)$ and $\text{O}({}^3P)$. The potential function for the dissociation of nitrous oxide must satisfy a number of conditions, among them being the following: (1) Removal of an oxygen atom to infinity must leave the function for a normal nitrogen molecule. (2) Removal of a nitrogen atom to infinity must reduce the potential to that of ${}^4\Sigma$ nitric oxide. (3) The minimum must correspond to the correct dissociation energy and interatomic distances. (4) It must yield the known vibration frequencies. A. E. Stearn and H. Eyring¹⁷ were able to devise a function that satisfied these conditions; utilizing the known interatomic distances and normal vibration frequencies, they constructed the potential-energy surface shown in Fig. 83. The angle between the axes is $58^\circ 54'$; and the reduction factor for r_2 , the N—N distance, is 0.968 in accordance with the requirements of Eqs. (9) and (10), Chap. III. According to this diagram, it appears that the molecule of nitrous oxide will remain in a hollow in the lower left corner, which represents the equilibrium state, until it acquires enough energy to travel up the valley parallel to the r_1 -axis, which represents dissociation into $\text{N}_2({}^1\Sigma)$ and $\text{O}({}^1D)$. Examination of the surface, however, does not indicate a maximum in the path over which the system has to travel, and so if it actually

¹⁷ A. E. Stearn and H. Eyring, *ibid.*, 3, 778 (1935).

followed this path the activation energy would be equal to the heat of dissociation, *i.e.*, about 90 kcal. The experimental energy of activation is, however, about 52 kcal., and the difference is accounted for by the fact that the $N_2(^1\Sigma) + O(^3P)$ surface cuts the one under consideration at a position well below that corresponding to the formation of 1D oxygen atoms.

It is now necessary to construct the surface for a 3P oxygen atom approaching a $^1\Sigma$ nitrogen molecule. At large distances the oxygen attracts the nearer nitrogen atom of the molecule by the van der Waals and coulombic forces, but it repels it by an

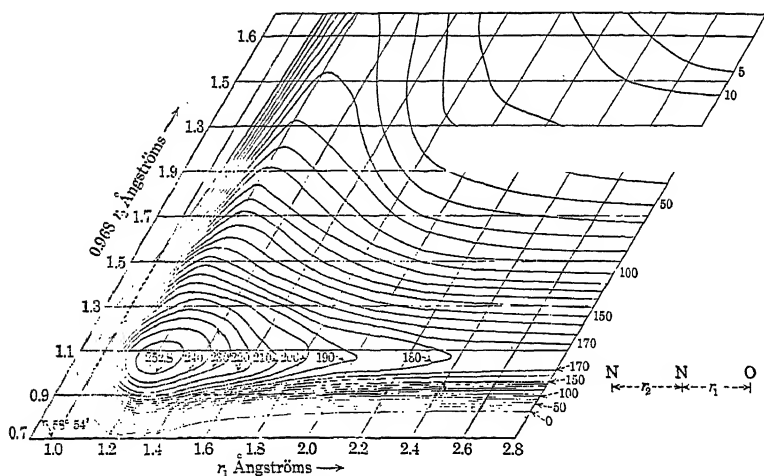
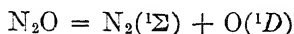


FIG. S3.—Potential-energy surface for the $N_2O(^1\Sigma) \rightarrow N_2(^1\Sigma) + O(^1D)$ reaction. (Stearn and Eyring.)

amount equal to one-half the sum of all the exchange integrals between the two atoms (see page 144). If the additive (coulombic) potential energy is taken as 0.14, *i.e.*, 14 per cent, of the Morse curve value for nitric oxide in its normal state and the repulsive energy as 0.43, *i.e.*, $\frac{1}{2}(1 - 0.14)$, of this value, then the *net repulsion* is 0.29 of the total energy as given by the Morse curve for normal nitric oxide. Each point on the repulsion curve for $N_2(^1\Sigma)$ and $O(^3P)$ is therefore obtained by taking -0.29 times the corresponding potential energy for nitric oxide. This gives the form of the required curve as a function of the N—O distance and its position, relative to the potential-energy surface for nitrous oxide dissociating into $N_2(^1\Sigma)$ and $O(^1D)$, is

found by the fact that the difference in energy between the 3P and 1D levels of atomic oxygen is known to be 45 kcal. The potential-energy profile for the dissociation



is obtained by taking a section of Fig. 83 passing through the bottom of the valley parallel to the r_1 -axis. This is shown by the curve in Fig. 84; on the same diagram is the repulsion curve

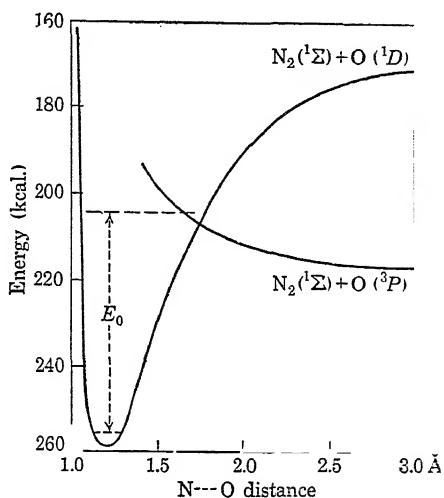


FIG. 84.—Crossing of potential-energy surfaces for $\text{N}_2(^1\Sigma) + \text{O}(^1D)$ and $\text{N}_2(^1\Sigma) + \text{O}(^3P)$. (Stearn and Eyring.)

for $\text{N}_2(^1\Sigma)$ and $\text{O}(^3P)$ obtained in the manner described above from the Morse curve for nitric oxide. Neglecting the resonance at the activated state, which is likely to be small in view of the electronic transition from a singlet to a triplet state, the point where the two curves cross gives the “classical” activation energy of the reaction as 52.8 kcal. The N—O distance in the activated complex is seen to be 1.73 Å. If the vibration frequencies in the normal and activated states are taken into consideration, it is found that E_0 is 50.0 kcal., whereas at a temperature of 900 to 1000°K. the value of E should be 52 kcal., which is in excellent agreement with the experimental value.

Reaction Rate and Transmission Coefficient.—According to M. Volmer, the rate of decomposition of nitrous oxide at rela-

tively high pressures can be expressed by the relationship¹⁸

$$k = 4.2 \times 10^9 e^{-53,000/RT} \text{ sec.}^{-1};$$

and so it is evident that if the entropy of activation has only a small negative value, as is very probable, the transmission coefficient κ must be approximately 10^{-4} ; if the value of κ were unity, the frequency factor would be of the order of 10^{13} , instead of 10^9 found experimentally. The statistical equation of the theory of absolute reaction rates reduces to

$$k = \kappa \left(\frac{I_{\ddagger}}{I_i} \right)^{1/2} \frac{\prod_4^3 (1 - e^{-h\nu_{\ddagger}^i/kT})^{-1}}{\prod (1 - e^{-h\nu_i/kT})^{-1}} \cdot \frac{kT}{h} e^{-E_0/RT}, \quad (47)$$

where the subscripts i and \ddagger refer to the initial and activated states, respectively. The normal vibration frequencies in the initial state are taken as 1,288.4, 2,224.1, and 589 (doubly degenerate) cm.^{-1} , whereas those in the activated state are found from the potential-energy function to be 2,005 and 361 (doubly degenerate) cm.^{-1} ; the moments of inertia are 6.67×10^{-39} and 10.14×10^{-39} g.cm.^2 for I_i and I_{\ddagger} , respectively. Upon taking E_0 as 51.2 kcal., obtained by subtracting the vibrational-energy terms from the experimental value of 52.0 kcal. for the energy of activation at about 940°K., the insertion of $k = 0.00192 \text{ sec.}^{-1}$ obtained by Nagasako and Volmer in Eq. (47) gives κ as

$$1.88 \times 10^{-4}.$$

If E_0 is taken as 50 kcal., as indicated by the potential-energy curves, then κ is found to be 3.5×10^{-4} . The transmission coefficient thus appears to be about 10^{-4} .

Use of the theory of nonadiabatic reactions outlined in Chap. III, together with the slope of the potential-energy curves at the point where they cross, a value of 10^{-4} for κ indicates that the separation between the resulting upper and lower surfaces should be as small as 5 cal. per mole. Of the many possible types of interaction capable of giving resonance energy ϵ of this magnitude, the only ones that appear probable are (1) inter-

¹⁸ M. Volmer and H. Kummerow, *Z. physik. Chem.*, **B**, **9**, 141 (1930); N. Nagasako and M. Volmer, *ibid.*, **B**, **10**, 414 (1930).

action of the spin of an electron in oxygen with its orbital magnetic moment; and (2) spin-spin interactions of the electrons inside the oxygen atom. An examination of the problem shows, however, that in neither case is the resonance energy of the correct value to account for the apparent transmission coefficient.

It is possible that a way out of the difficulty may be found in the conclusion that the activation energy for the dissociation of nitrous oxide is several thousand calories greater than the value of 53 kcal. given above¹⁹; if this is the case, the frequency factor would be increased by 10^2 to 10^3 to account for the observed reaction rate, and κ would be as high as 10^{-1} to 10^{-2} . In any case, the dissociation of nitrous oxide is pseudo-unimolecular, and hence the transmission coefficient would be less than unity if the transfer of energy to the reacting molecule in a collision were a slow process, as explained in Chap. V. If the low value of κ were due to this cause, it should approach unity at higher pressures; this may be one of the factors responsible for the unusual phenomena associated with the dissociation of nitrous oxide at high pressures.

QUENCHING OF FLUORESCENCE

Quenching in Solution.—It is generally accepted that the quenching of fluorescence is brought about by the transfer of electronic energy from the excited molecule to kinetic energy of the quenching molecule in a collision between the two. There is evidence that in solution, at least, the quenching process involves more than mere collision; it appears that a definite activated complex is formed between the fluorescing and quenching species, and the rearrangement of energy presumably occurs within this complex. Measurements on the quenching of fluorescence by ions in solution show the process to be bimolecular, and the variation of the reaction rate with ionic strength is in agreement with that found for chemical interaction.²⁰ It will be shown in Chap. VIII that, for an ionic reaction in dilute

¹⁹ Cf. R. F. Hunter, *Proc. Roy. Soc.*, **144**, A, 386 (1934); R. M. Lewis and C. N. Hinshelwood, *ibid.*, **168**, A, 441 (1938); C. N. Hinshelwood, *Trans. Faraday Soc.*, **24**, 70 (1938).

²⁰ R. W. Stoughton and G. K. Rollefson, *J. Am. Chem. Soc.*, **61**, 2634 (1939); see also *idem*, *ibid.*, **62**, 2264 (1940).

solution, the specific reaction rate k depends on the ionic strength μ of the medium and is given by

$$\log k = \log k_0 + 1.02z_A z_B \sqrt{\mu}, \quad (48)$$

where z_A and z_B are the valences of the reacting species. The rates of quenching of the fluorescence of quinine sulfate ($z = 2$), fluorescein and acridone ($z = 0$) and anthracene sulfonic acid ($z = -1$) by various ions have been shown to vary with the ionic strength in accordance with the requirements of Eq. (48).

The requirement of the formation of a definite activated complex in these particular cases of the quenching of fluorescence is in harmony with the conclusions reached in other instances of the transfer of energy in gas reactions (*cf.* pages 112 to 115). It is probable that the variations in the so-called "quenching radii," or "quenching cross sections," of various molecules could be explained by the variation of the interaction between the excited molecule and the quenching substance.

It should be mentioned that the actual quenching process in solution is often so rapid that the rate-determining step in the over-all reaction is the diffusion of the molecules toward one another. The rate is then a function of the diffusion constants and hence of the viscosity of the medium.²¹

²¹ *Cf.* J. M. Franck and S. J. Wawilow, *Z. Physik*, **69**, 100 (1931); B. Sveshnikow, *Acta Physicochim. U.R.S.S.*, **3**, 357 (1935); **4**, 453 (1936).

CHAPTER VII

HETEROGENEOUS PROCESSES

Many reactions involving gases are known to occur more rapidly as heterogeneous processes on the surface of a solid, which acts as a catalyst, than as homogeneous reactions in the gas phase. It is generally agreed that the primary function of the catalyst is to adsorb the reacting molecules, with the result that the reaction can now take place by a more economical reaction path, requiring a smaller activation energy than the corresponding homogeneous process. Since adsorption of the gases must play an important part in heterogeneous gaseous reactions, this subject will be given some consideration.

ADSORPTION

The van der Waals and Activated Adsorption.—It has been accepted for some years that there are two main types of adsorption of gases by solids. The first, known as the van der Waals adsorption, involves forces of a physical nature, such as the "dispersion forces" discussed by F. London (1930); but in the second type, sometimes referred to as "chemisorption," the forces concerned are similar to those taking part in ordinary chemical bond formation. Adsorption of the van der Waals type is generally accompanied by small heat changes, *e.g.*, 5 kcal., or less, per mole, whereas the heat evolved in chemisorption is of the order of the amounts concerned in chemical reactions, *viz.*, 10 to 100 kcal. per mole of gas adsorbed. It was pointed out by H. S. Taylor¹ that adsorption of the latter type is frequently a slow process associated with appreciable heat of activation and hence may be called "activated adsorption." In view of the relatively high heats of activation, which are frequently of the order of 20 kcal., activated adsorption will naturally take place slowly at low temperatures; under these conditions the van der Waals adsorption will predominate,

¹ H. S. Taylor, *J. Am. Chem. Soc.*, **53**, 578 (1931); *Chem. Rev.*, **9**, 1 (1931).

for this requires very little activation energy. As the temperature is raised, the rate of activated adsorption should increase, and its extent should become appreciable.

The difference between the van der Waals and activated adsorption can be readily explained with the aid of a potential-energy diagram. As the gas molecule is brought up to the surface from a distance, there is a small van der Waals attraction, as shown by the slight dip in curve I in Fig. 85; any attempt to decrease the distance of separation below the equilibrium value for the van der Waals adsorption leads to gradually increasing repulsion. If there is a possibility of more intimate, *i.e.*, chemical, association between the gas and the surface, there will be another potential-energy curve, *viz.*, II in Fig. 85; and the

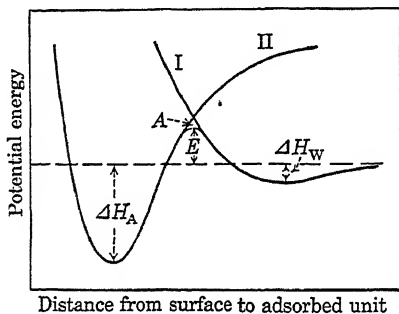


FIG. 85.—Potential-energy curves for van der Waals and activated adsorption.

minimum of this curve represents the equilibrium state for activated adsorption. The change from the van der Waals to activated adsorption occurs at the crossing point of curves I and II, somewhat rounded off on account of resonance, at A; and the energy at this point, in excess of that for the separated metal and gas molecule, is the activation energy E for the latter type of adsorption. The heats of adsorption are indicated by ΔH_W and ΔH_A for the van der Waals and activated adsorption, respectively. The fact that the extreme right-hand of curve II is above that of I implies that the process of activated adsorption is accompanied by partial or complete dissociation of the molecule of adsorbed gas. The energy difference between the horizontal portions of the two curves is equal to the heat of dissociation taking place in activated adsorption. It has been assumed in this discussion that the gas under consideration is

capable of undergoing activated adsorption; if it were not, *e.g.*, one of the inert gases of the atmosphere, there would be no potential-energy curve corresponding to II in Fig. 85.

The concept of activated adsorption provides a satisfactory explanation of many phenomena associated with adsorption; for example, the heat of adsorption is often small at low temperatures but becomes large at higher temperatures. This is due to the fact that the van der Waals adsorption is the dominating factor under the former conditions, whereas activated adsorption, or chemisorption, accompanied by large heat changes, becomes more important as the temperature is raised. The actual rates of adsorption of gases are frequently high at low temperatures, *e.g.*, hydrogen on a mixture of manganese and chromic oxides at -78°C ., but are relatively low on the same adsorbent at higher temperatures.² The curious variations often observed in the amount of adsorption with changing temperature³ (Fig. 86)

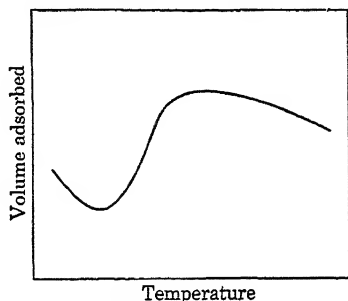


FIG. 86.—Variation of amount adsorption with temperature.

are explained in the following manner. Since adsorption is an exothermic process, the extent should decrease with increasing temperature, and this is true of the van der Waals adsorption at the lowest temperatures. As the temperature is raised, however, the rate of activated adsorption and the amount adsorbed in this manner during the course of the experiment increase, so that there is an increase in the total adsorption. At still higher temperatures the normal decrease in the extent of activated adsorption with rising temperature becomes manifest.

Although the adsorption of hydrogen on tungsten powder is a slow process that increases with temperature and hence appears to require a definite activation energy,⁴ it has been suggested that no such activation energy is associated with the adsorption on a *clean* surface of the same metal.⁵ The rate of adsorption

² H. S. Taylor and A. T. Williamson, *J. Am. Chem. Soc.*, **53**, 813 (1931).

³ See, for example, A. W. Gauger and H. S. Taylor, *ibid.*, **45**, 920 (1923)

⁴ W. Frankenburger and A. Hodler, *Trans. Faraday Soc.*, **28**, 229 (1932).

⁵ J. K. Roberts, *Proc. Roy. Soc.*, **152**, A, 445 (1935).

appears to be almost independent of temperature, and so it has been concluded that the adsorption of hydrogen on tungsten requires no energy of activation; if the surface is covered with oxygen, however, it is believed that an energy of activation is concerned in the adsorption. It will be seen later (page 353) that there is some doubt concerning the conclusion that the rate of adsorption is independent of temperature; but even if the energy of activation for adsorption on tungsten were zero, the results throw no light on the nature of the adsorption of hydrogen on other metals, *e.g.*, nickel, copper and iron, or on certain oxides for which an energy of activation is believed to be involved.⁶

Calculation of Activation Energies.—An attempt to calculate the energy of activation accompanying the chemisorption of hydrogen on carbon, using the method for constructing the potential-energy surface described in Chap. III, has been made

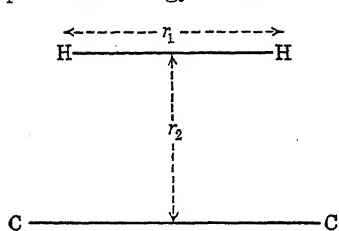
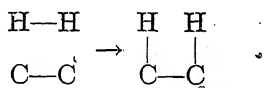


FIG. 87.—Symmetrical approach of hydrogen molecule to two carbon atoms fixed on the surface.

in the following manner.⁷ The reaction between a molecule of hydrogen and a carbon surface may be represented as



and the potential energy, if the system is treated as a four-electron problem, may be calculated approximately by the London equation. The Morse functions for H—H, C—C and C—H are known; and, on the assumption of 10 per cent coulombic energy, it is possible to construct a potential-energy surface for a definite C—C distance. In order to simplify the calculations the hydrogen molecule is supposed to approach the two carbon atoms in such a manner as to keep the system always symmetrical about the perpendicular bisector of the line joining

⁶ H. S. Taylor *et al.*, *J. Am. Chem. Soc.*, **53**, 813 (1931); **54**, 602 (1932); **56**, 1178, 2259 (1934); *Trans. Faraday Soc.*, **30**, 1178 (1934); A. F. Benton, *ibid.*, **28**, 209 (1932); P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **56**, 35 (1934); P. H. Emmett and R. W. Harkness, *ibid.*, **57**, 1631 (1935); see also O. I. Leypunsky, *Acta Physicochim. U.R.S.S.*, **2**, 737 (1935); *J. Chem. Phys. Russ.*, **9**, 143 (1937).

⁷ A. Sherman and H. Eyring, *J. Am. Chem. Soc.*, **54**, 2661 (1932).

these atoms. The potential energy can then be expressed as a function of two parameters (see Fig. 87), *viz.*, the distance between the two hydrogen atoms (r_1) and that between the

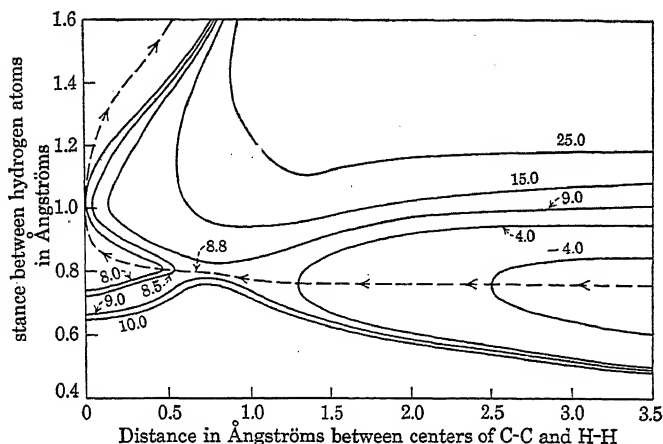


FIG. 88.—Potential-energy surface for adsorption of a hydrogen molecule on two carbon atoms. (Sherman and Eyring.)

centers of the two carbon and two hydrogen atoms (r_2), a definite value for the C—C distance being assumed; the essential features of the surface are shown by the typical example in Fig. 88. The

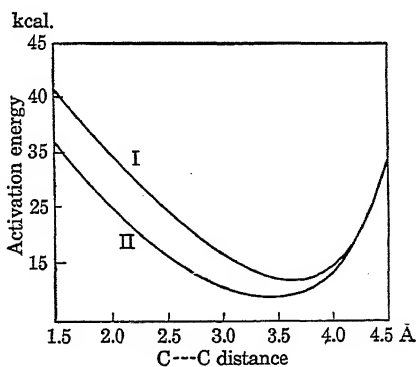
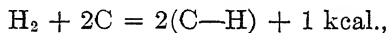


FIG. 89.—Dependence of activation energy for adsorption of a hydrogen molecule on the C—C distance. (Sherman and Eyring.)

activation energies for the adsorption of hydrogen on carbon for a series of C—C distances from 1.5 to 4.5 Å. were obtained in a similar manner and the results plotted in Fig. 89, curve I; it is seen that a minimum occurs at 3.6 Å., and this should repre-

sent the most favorable separation between the carbon atoms on a surface for the adsorption of hydrogen.

In the calculations described above the potential-energy curves used were those which gave satisfactory calculated values for the energies of activation for the hydrogenation of ethylene and acetylene. This procedure is, however, not completely satisfactory; for there is reason to believe that the C—H bonds formed in the adsorption process are appreciably weaker than ordinary C—H bonds which require 96 kcal. for dissociation. Suppose the adsorption process involved the breaking of a H—H bond and a C—C bond, requiring 103 kcal. and 70 kcal., respectively, and their replacement by two C—H bonds; if the latter were ordinary bonds, the heat evolved in adsorption would be $2 \times 96 - (103 + 70)$, *i.e.*, 19 kcal. Although the H—H bond is broken, the C—C bonds are not; and so the heat of adsorption for this particular mechanism should be much greater than 19 kcal. The experimental value is, however, about 1 kcal.; it is thus probable that the C—H bonds are much weaker than those normally existing in an organic compound. An estimate of the bond energy may be made in the following manner. According to experiment,



where 2C represents two carbon atoms on the surface and C—H implies the adsorption of a hydrogen atom. Since the heat of dissociation of molecular hydrogen is 103 kcal., the energy of the C—H bond will be $\frac{1}{2}(103 + 1)$, *i.e.*, 52 kcal. The calculations of the activation energy for adsorption were, therefore, repeated using a value of 52 kcal. for the C—H bond formed in adsorption; the results are depicted in Fig. 89, curve II. The change introduced by the altered strength of the C—H bond is not very great, and it is of interest to note that the C—C distance of 3.6 Å. is still the most favorable for adsorption of hydrogen. The potential-energy surface shown in Fig. 88 is the actual one for these conditions, on the assumption of 10 per cent coulombic energy; the activation energy is seen to be 8.8 kcal. By taking the coulombic energies of the C—H and C—C bonds as 14 per cent of the total, an activation energy in better agreement with experiment is obtained for the reaction between ethylene and hydrogen; and the same proportion gives

5.6 kcal. for the activation energy for the adsorption of hydrogen on carbon.

It may be somewhat unexpected, at first sight, that this optimum distance is considerably larger than the normal H—H separation in molecular hydrogen; the reason for this may be seen qualitatively in the following manner. Consider the case in which the C—C distance is the same as the normal H—H distance in molecular hydrogen, as shown in Fig. 90; there is a large interaction between H (1) and C (2) and between H (2) and C (1), so that the γ terms in the London equation are relatively large. As seen in Chap. III, this will lead to a relatively high activation energy. In the extreme case, where the carbon atoms are very far apart, the reaction would virtually involve the dissociation of the hydrogen molecule and the activation energy would again be large. The interatomic C—C distance of 3.6 Å. evidently provides the best compromise and gives the minimum activation energy.

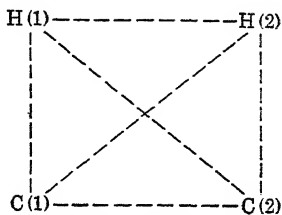


FIG. 90.—Carbon atoms on surface separated by the normal internuclear distance in molecular hydrogen.

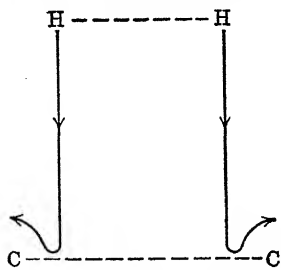


FIG. 91.—Path of hydrogen molecule approaching carbon atoms on the surface.

An examination of Fig. 88 reveals another result of some interest; it will be seen that as the hydrogen approaches the surface, the distance between the hydrogen atoms remains unchanged until the molecule is quite close to the line joining the carbon atoms. A slight extension occurs but the hydrogen molecule must apparently reach the C—C axis before there is appreciable expansion; the hydrogen atoms now move away from the surface until they occupy their equilibrium positions as shown in Fig. 91. During this process of separation of the hydrogen atoms the C—H distance remains almost unchanged. The process of desorption of hydrogen from carbon will, of course, be represented by the reverse of the path depicted in Fig. 91.

Calculations of the activation energy for the adsorption of hydrogen on nickel have also been made;⁸ on the assumption

⁸ A. Sherman, C. E. Sun and H. Eyring, *J. Chem. Phys.*, **3**, 49 (1934).

that the proportion of coulombic binding is 14 per cent in the H—H bond, 20 per cent for Ni—H and 30 per cent for Ni—Ni (cf. page 84), an activation energy for hydrogen adsorption of 24 kcal. was obtained, for a Ni—Ni separation of 2.38 Å. on the surface. The heat of adsorption for the same model was found to be 4.6 kcal., which is probably lower than the true value. Strictly speaking, two different Ni—Ni distances, *viz.*, 2.49 and 3.52 Å., are possible, as may be seen from the lattice planes represented in Fig. 92, and the activation energy for adsorption of hydrogen has been calculated for both these distances;⁹ the coulombic energy was taken as 11 per cent of the total binding energy for H—H, 37 per cent for Ni—Ni¹⁰ and 24 per cent, the mean of the other two values, for the Ni—H bond. The activation energy obtained for the 2.49 Å. separation was

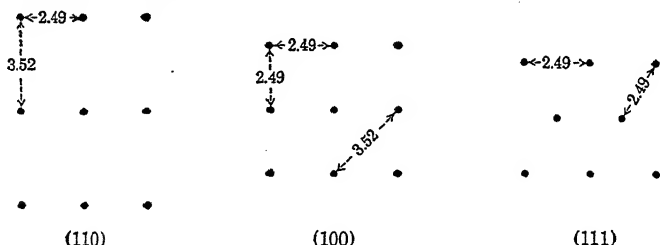


FIG. 92.—Representation of lattice planes in a nickel crystal.

75 kcal.; that for 3.52 Å. was 57 kcal. It is evident that hydrogen atoms will become adsorbed preferentially on atoms separated by 3.52 Å., and hence adsorption should occur primarily on the (100) and (110) planes. Although the calculated activation energies are undoubtedly too high, the general conclusion appears to be supported by the work of O. Beeck *et al.*,¹¹ it has been found that the catalytic activity for the hydrogenation of ethylene on a nickel surface film in which the (110) planes of the crystal are oriented parallel to the supporting material is five times as great as that for a film having randomly oriented crystals. It is possible that the special properties of active

⁹ G. Okamoto, J. Horiuti and K. Hirōta, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **29**, 223 (1936).

¹⁰ Cf. N. Rosen and S. Ikehara, *Phys. Rev.*, **43**, 5 (1933).

¹¹ O. Beeck, A. Wheeler and A. E. Smith, *Phys. Rev.*, **55**, 601 (1939); A. E. Smith and O. Beeck, *ibid.*, **55**, 602 (1939); *Proc. Roy. Soc.*, **177**, A, 62 (1940); see also G. H. Twigg and E. K. Rideal, *Trans. Faraday Soc.*, **36**, 533 (1940).

centers and the influence of promoters may be determined by the lattice spacings in the catalytic surface.¹²

Rate of Adsorption and Theory of Absolute Reaction Rates.—An adsorption process may be considered simply as a bimolecular reaction involving a molecule or atom from the gas phase and an atom of the solid or, in general, an active point occupying a fixed position on the adsorbing surface.¹³ Reaction, *i.e.*, adsorption, then involves the formation of an activated complex between the gas molecule and the point on the surface, and the rate of the process is given, in the usual manner (see page 187), by the rate of passage of this complex over a potential-energy barrier. The height of the barrier is, of course, the energy of activation for adsorption. In the most general case, the adsorbing centers on the surface will not all have the same activity and hence may be regarded as consisting of several types; the centers belonging to each type will have a characteristic potential-energy surface and their own heat and entropy of adsorption.

Consider the adsorption sites of a particular type: at any given instant in the course of adsorption, their number is supposed to be N_s , but this will diminish as the surface becomes covered to an increasing extent. Let N_g be the number of molecules in the gas phase, and $N_‡$ the number of activated complexes on the sites under consideration; if V cc. is the volume of the gas phase and S sq. cm. the area of the surface, then

Concentration in gas phase, $c_g = N_g/V$ molecules per cc.

Concentration of adsorption centers, $c_s = N_s/S$ sites per sq. cm.

Concentration of activated complexes, $c_‡ = N_‡/S$ molecules per sq. cm.

According to the postulates of the theory of absolute reaction rates an equilibrium may be supposed to exist between molecules of gas, adsorption centers and activated complexes, so

¹² Cf. R. W. G. Wyckoff and E. D. Crittenden, *J. Am. Chem. Soc.*, **47**, 2866 (1925); R. E. Burk, *J. Chem. Phys.*, **30**, 1134 (1926); A. A. Balandin, *Z. physik. Chem.*, **B**, **2**, 289 (1929); **B**, **3**, 167 (1929); see also H. S. Taylor, "Twelfth Report of the Committee on Catalysis: National Research Council," p. 47, John Wiley & Sons, Inc., 1940.

¹³ K. J. Laidler, S. Glasstone and H. Eyring, *J. Chem. Phys.*, **8**, 659 (1940); see also G. E. Kimball, *ibid.*, **6**, 447 (1938); M. Temkin, *Acta Physicochim. U.R.S.S.*, **8**, 141 (1938).

that, provided that the various components of the system behave ideally,

$$K = \frac{c_{\ddagger}}{c_g c_s} = \frac{N_{\ddagger}}{(N_g/V)N_s} \quad (1)$$

$$= \frac{f_{\ddagger}'}{(f_g/V)f_s} \quad (2)$$

where the f terms are the complete partition functions of the indicated species. If F_g represents the partition function for *unit volume* of the gas undergoing adsorption, *i.e.*,

$$F_g = \frac{f_g}{V}, \quad (3)$$

then it follows from Eqs. (1) and (2) that

$$\frac{c_{\ddagger}}{c_g c_s} = \frac{f_{\ddagger}'}{F_g f_s} \quad (4)$$

and hence

$$c_{\ddagger} = c_g c_s \frac{f_{\ddagger}'}{F_g f_s}. \quad (5)$$

According to the theory of absolute reaction rates, the rate of adsorption of gas on sites of the i th kind per square centimeter is given by

$$v_{1(i)} = c_g c_{s(i)} \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g f_s}, \quad (6)$$

where f_{\ddagger} differs from f_{\ddagger}' in the usual manner (page 189) by the removal from the latter of the contribution to the partition function of the degree of translational freedom in the reaction coordinate. If the surface were uniform and all the adsorbing centers had equal activity, c_s would represent the *total* number of bare sites per square centimeter, and f_{\ddagger} and f_s would be applicable to all activated complexes and adsorbing centers, respectively; the resultant rate of adsorption over the whole surface would then be

$$v_1 = c_g c_s \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g f_s}. \quad (7)$$

If the zero-point energy contribution is extracted from the partition functions (*cf.* page 188), Eq. (7) becomes

$$v_1 = c_g c_s \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g f_s} e^{-\epsilon_1/kT} \quad (8)$$

where ϵ_1 is the energy of activation for adsorption per single molecule at the absolute zero; the value of the energy in the partition function for each species is now reckoned from its own zero-point level. If the surface is nonuniform, Eq. (8) may still be regarded as applicable, but f_{\ddagger} , f_s and ϵ_1 will be weighted averages for all the types of adsorbing centers on the surface; it will be seen later that f_{\ddagger}/f_s is approximately unity for an immobile adsorbed layer, and so the only effective correction necessary is in the activation energy (see page 394).

Immobile Adsorbed Layers.—In the foregoing treatment the adsorption centers on the surface have been regarded as reactants, and hence it is implied that every adsorbed molecule uses up one active center. This is equivalent to saying that the gas adsorbed on the surface forms an immobile layer; *i.e.*, a molecule is assumed to stay wherever it is adsorbed until it is desorbed. The translational contribution to the partition function of the activated state f_{\ddagger} is thus unity; and the remainder, due to vibration and rotation, may be represented by b_{\ddagger} . Further, the adsorption centers are presumably atoms of the metal, or other substance, constituting the surface, and they probably have vibrational energy only; hence, the partition function f_s may be taken as unity. Substitution of these values in Eq. (8) gives

$$v_1 = c_g c_s \frac{kT}{h} \cdot \frac{b_{\ddagger}}{F_g} e^{-\epsilon_1/kT} \quad (9)$$

$$= c_g c_s \frac{kT}{h} \cdot \frac{b_{\ddagger}}{(2\pi m kT)^{3/2}} e^{-\epsilon_1/kT}, \quad (10)$$

where F_g , the partition function of the gas for unit volume, is split up into the translation contribution for three degrees of freedom, $(2\pi m kT)^{3/2}/h^3$, and the vibrational and rotational factors, represented by b_g . It is probable, in view of the immobility of the activated complex, that there will be no rotation in this state; hence, b_{\ddagger} will be virtually a vibrational partition function, and its value may be taken as unity, apart from a

symmetry factor. Similarly, the vibrational part of b_g will not differ greatly from unity, and hence b_g can be replaced by the rotational contribution, *i.e.*, $8\pi^2 I kT / h^2 \sigma$ for a diatomic molecule; Eq. (10) then becomes

$$v_1 = c_g c_s \frac{kT}{h} \cdot \frac{1/\sigma_{\ddagger}}{\frac{(2\pi m kT)^{3/2}}{h^3} \cdot \frac{8\pi^2 I kT}{h^2 \sigma}} e^{-\epsilon_1/kT}, \quad (11)$$

where σ and σ_{\ddagger} are the symmetry factors of the gas molecule and of the activated complex, respectively, or

$$v_1 = c_g c_s \frac{\sigma}{\sigma_{\ddagger}} \cdot \frac{h^4}{8\pi^2 I (2\pi m kT)^{3/2}} e^{-\epsilon_1/kT}. \quad (12)$$

So far it has been assumed that in the formation of the activated state the gas molecule attaches itself to one adsorption center only; this will be the case for monatomic molecules, and possibly for more complicated molecules in certain instances, but in many cases two adjacent sites are required for adsorption. Under these circumstances, Eq. (12) will still give the rate of adsorption if c_s now represents the number of such dual sites per square centimeter, and this may be related to the number of single adsorption centers in the following manner. Each site will have a certain number, say s , adjacent sites, so that the total number of dual sites will be $\frac{1}{2} s c_s$, the factor $\frac{1}{2}$ arising from the fact that otherwise each pair is counted twice. The initial rate of adsorption of a gas molecule requiring two centers is thus $\frac{1}{2} s$ times the rate given by Eq. (12), *i.e.*,

$$v_1 = \frac{1}{2} s c_g c_s \frac{\sigma}{\sigma_{\ddagger}} \cdot \frac{h^4}{8\pi^2 I (2\pi m kT)^{3/2}} e^{-\epsilon_1/kT}, \quad (13)$$

where c_s still represents the number of single adsorption centers per square centimeter. It will be shown later that this equation may also be valid when dissociation accompanies adsorption.

Mobile Adsorbed Layer.—It is of interest to compare this result with that which would be obtained if the molecules were mobile in the adsorbed state, and hence presumably also in the activated state. The adsorption centers need no longer be regarded as reactants, the activated complex being the gas molecule just before it strikes the surface. The equilibrium

between initial and activated states may thus be represented [cf. Eqs. (1) and (2)] by

$$K = \frac{c_{\ddagger}}{c_g} = \frac{N_{\ddagger}/S}{N_g/V} = \frac{F_{\ddagger}'}{F_g}, \quad (14)$$

where F_g and F_{\ddagger}' are the partition functions for unit volume of gas and per square centimeter of activated complex, respectively; by the methods used in the case of immobile molecules, it follows that

$$v_1 = c_g \frac{kT}{h} \cdot \frac{F_{\ddagger}}{F_g} e^{-\epsilon_1/kT}. \quad (15)$$

Since the activated complex is still in the gaseous state, it will have vibrational and rotational degrees of freedom similar to the initial gas molecules; hence the ratio of the partition functions F_{\ddagger}/F_g reduces to the ratio of the translational terms. In the activated state the molecule has only two degrees of translational freedom, *i.e.*, over the surface, whereas in the gaseous state it has three such degrees of freedom. The values of F_{\ddagger} and F_g are therefore $(2\pi mkT)/h^2$ and $(2\pi mkT)^{3/2}/h^3$, respectively; it follows, therefore, that

$$v_1 = c_g \frac{kT}{h} \cdot \frac{h}{(2\pi mkT)^{1/2}} e^{-\epsilon_1/kT}. \quad (16)$$

If $c_g kT$ is replaced by the pressure p of the gas, to which it is equivalent if the latter is ideal, then, in the special case of adsorption requiring no activation energy, Eq. (16) becomes

$$v_1 = \frac{p}{(2\pi mkT)^{1/2}}. \quad (17)$$

This result is identical with the classical Hertz-Knudsen equation for the number of gas molecules striking 1 sq. cm. of a surface in unit time; it would also give the rate of adsorption provided that the adsorbed layer were mobile and there were no activation energy of adsorption.

Test of Adsorption Equations.—In order to test the validity of the equations based on the theory of absolute reaction rates, it would be necessary to have reliable data for the rates of adsorption of gases on surfaces of known area; unfortunately, such data are very scanty. All the examples that will be con-

sidered here refer to adsorption processes that involve the dissociation of the diatomic gas on adsorption, but it will be shown later that Eq. (13) is generally applicable to such processes.

An approximate comparison of observed and calculated rates of adsorption has been made by M. Temkin,¹⁴ who derived an expression similar to Eq. (13); he showed that the measurements of O. I. Leypunsky¹⁵ were in general agreement with those to be expected from the theory of absolute reaction rates for an immobile adsorbed layer. A more precise comparison can be made using P. H. Emmett's data for the adsorption of nitrogen and hydrogen on an iron-aluminum oxide catalyst (the so-called "catalyst 931").¹⁶ The surface area of such a catalyst cannot be determined by direct measurement, but a reliable estimate can be made from the curve showing the amount of gas adsorbed against time. In Table XXXIX are given the observed and

TABLE XXXIX.—CALCULATED AND OBSERVED RATES OF ADSORPTION

Gas	Temp., °K.	<i>E</i> , kcal.	Rate of adsorption	
			Calc.	Obs.
N ₂	544	14.4	35.8×10^{16}	3.4×10^{16}
H ₂	194.5	10.4	5.7×10^{15}	1.8×10^{17}

calculated rates for approximately half-covered surfaces, expressed as molecules per second on the surface present in the experiment. The agreement is seen to be satisfactory on the whole; it is probable that the recorded activation energy (10.4 kcal. per mole) for the adsorption of hydrogen is too high, and a value of 8.9 kcal. would give almost exact correspondence between observed and calculated rates of adsorption.

It appeared possible, at first sight, that the data obtained by J. K. Roberts¹⁷ for the rate of adsorption of hydrogen on a clean tungsten wire of known area might provide a satisfactory test of Eq. (13), but there may be some doubt concerning the

¹⁴ Temkin, Ref. 13.

¹⁵ Leypunsky, Ref. 6.

¹⁶ Emmett and Brunauer, Ref. 6; Emmett and Harkness, Ref. 6.

¹⁷ Roberts, Ref. 5.

reliability of the results obtained. Application of the equation, on the assumption that each molecule of hydrogen is adsorbed on two centers and s being taken as equal to 4 and c_s as 10^{15} sites per square centimeter, gives the rate of adsorption as $9.84 \times 10^{17} e^{-E_1/RT}$ molecules per sq. cm. per sec. for a pressure of 10^{-4} mm. at 79°K .; this value may be compared with the maximum rate of adsorption of 5.9×10^{12} molecules per sq. cm. per sec. derived from the measurements of Roberts. The calculated and observed rates would agree if the activation energy for adsorption were about 2.0 kcal.; but since the experiments show that the rates of adsorption are almost the same at 79° and 295°K ., the activation energy should be zero. Another possibility is that only one site in about 10^5 can act as an adsorption center in the rate-determining stage, but this would seem to be unlikely. The discrepancy of 10^5 between calculated and experimental rates of adsorption is, therefore, difficult to understand, particularly in view of the satisfactory agreement obtained in other instances. It is possible, however, that in the work with hydrogen on tungsten the rate measured was not that of adsorption, but of another process, such as the rate of access of hydrogen to the surface under the experimental conditions.* If this is so, the conclusion that the rate of adsorption is independent of temperature and that the activation energy for adsorption is thus zero is open to doubt; the activation energy for adsorption might be as high as 2 kcal. and the adsorption process still be faster than the over-all observed rate.

Rate of Desorption.—The variation with pressure of the amount of gas adsorbed by a solid at constant temperature has been represented by the empirical classical isotherm or by the familiar equation first deduced by I. Langmuir¹⁸ on the basis of a kinetic interpretation of adsorption of a single layer of gas molecules. The same result has been obtained by M. Volmer,¹⁹ who assumed the adsorbed molecules to be mobile, and by

* Somewhat similar suggestions were considered in a footnote to p. 76 of a preliminary paper by J. K. Roberts [*Proc. Cambridge Phil. Soc.*, **30**, 76 (1933–1934)].

¹⁸ I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916); **40**, 1361 (1918).

¹⁹ M. Volmer, *Z. physik. Chem.*, **115**, 253 (1925); see also G. S. Rushbrooke and C. A. Coulson, *Proc. Cambridge Phil. Soc.*, **36**, 248 (1940) for a thermodynamic derivation for an immobile layer.

R. H. Fowler²⁰ using statistical methods. The same isotherm is derived below from the theory of absolute reaction rates.

Desorption from an immobile layer may be regarded as involving an activated state in which a molecule attached to an adsorption center acquires the necessary configuration and activation energy to permit it to escape from the surface. As a result of the equilibrium between adsorbed and activated molecules, it follows that if N_a and N_{\ddagger} are the numbers of adsorbed molecules and of activated complexes and c_a and c_{\ddagger} are their respective concentrations, in molecules per square centimeter, then

$$K = \frac{c_{\ddagger}}{c_a} = \frac{N_{\ddagger}/S}{N_a/S} = \frac{f_{\ddagger}'}{f_a}, \quad (18)$$

and hence

$$c_{\ddagger} = c_a \frac{f_{\ddagger}'}{f_a}, \quad (19)$$

the f terms being the complete partition functions. According to the theory of absolute reaction rates, the rate of desorption v_2 , per square centimeter of surface per second, is given by

$$v_2 = c_a \frac{kT}{h} \cdot \frac{f_{\ddagger}}{f_a}, \quad (20)$$

where f_{\ddagger} no longer includes the partition function for translation across the potential-energy barrier. If the difference of the zero-level energies is extracted, it follows that

$$v_2 = c_a \frac{kT}{h} \cdot \frac{f_{\ddagger}}{f_a} e^{-\epsilon_2/kT}, \quad (21)$$

where ϵ_2 represents the energy of activation for the desorption of a single molecule at the absolute zero.

This equation may be tested by the data on the rates of desorption of carbon monoxide from platinum and of oxygen from tungsten.²¹ If both the activated complexes and adsorbed molecules are assumed to be immobile, the ratio of the partition

²⁰ R. H. Fowler, *ibid.*, **31**, 260 (1935); R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," p. 426, Cambridge University Press, 1939.

²¹ I. Langmuir, *Trans. Faraday Soc.*, **17**, 641 (1922); I. Langmuir and D. S. Villars, *J. Am. Chem. Soc.*, **51**, 486 (1931).

functions f_{\pm}/f_a should be approximately equal to unity; hence, if the rate of desorption is expressed in the general form

$$v_2 = Be^{-E_2/RT},$$

where E_2 is the activation energy for desorption per mole of gas, B should be equal to $c_a(kT/h)$ by Eq. (21). For a surface that is almost completely covered, c_a may be taken as 10^{15} molecules per sq. cm., and so the rate of desorption may be calculated; the values of B obtained in this manner are compared in Table XL

TABLE XL.—CALCULATED AND OBSERVED RATES OF DESORPTION

Gas	Surface	Temp., °K.	E , kcal.	Rate of desorption	
				B (calc.)	B (obs.)
CO	Pt	600	32.0	1.25×10^{28}	2.79×10^{29}
O ₂	W	2000	165.0	4.16×10^{28}	13.4×10^{30}

with those derived experimentally, the rates being expressed as molecules becoming desorbed per square centimeter per second. The difference between observed and calculated values for carbon monoxide is not serious, but with oxygen it is greater than would be expected. It must be remembered that there may well be more rotational and vibrational freedom in the activated than in the adsorbed state, and this would tend to make the partition-function factor greater than unity; the calculated rate of desorption would then be larger than is given in Table XL.

The Adsorption Isotherm.—For adsorption equilibrium at any temperature, the rates of adsorption and of desorption, as given by Eqs. (8) and (21), must be equal; hence,

$$c_a c_s \frac{kT}{h} \cdot \frac{f_{\pm}}{F_g f_s} e^{-\epsilon_1/kT} = c_a \frac{kT}{h} \cdot \frac{f_{\pm}}{f_a} e^{-\epsilon_2/kT} \quad (22)$$

$$\therefore \frac{c_a}{c_s} = c_g \frac{f_a}{F_g f_s} e^{\epsilon/kT} \quad (23)$$

where ϵ , which is equal to $\epsilon_2 - \epsilon_1$, is the heat (evolved) of adsorption per single molecule at 0°K. If θ is the fraction of the adsorption centers that are covered by adsorbed molecules, $1 - \theta$ is the fraction still bare at any instant, and

$$\frac{c_a}{c_s} = \frac{\theta}{1 - \theta} \quad (24)$$

hence, by Eq. (23),

$$\frac{\theta}{1 - \theta} = c_g \frac{f_a}{F_g f_s} e^{\epsilon/kT}. \quad (25)$$

As seen above, f_s may be taken as unity, and F_g may be represented by

$$F_g = \frac{(2\pi m kT)^{3/2}}{h^3} b_g. \quad (26)$$

Further, since the adsorbed molecules are supposed to be immobile, the partition function f_a may be replaced by b_a , the contribution of the internal degrees of freedom. Finally, upon writing p/kT for c_g in Eq. (25), the latter becomes

$$\frac{a}{1 - \theta} = p \frac{h^3}{(2\pi m)^{3/2} (kT)^{3/2}} \cdot \frac{b_a}{b_g} e^{\epsilon/kT}, \quad (27)$$

which is identical with the expression derived by Fowler. This relationship may be written as

$$\frac{\theta}{1 - \theta} = ap, \quad (28)$$

where, for a given system, a is a function of the temperature only; Eq. (28) is, in fact, an isotherm identical with that of Langmuir, as may be seen by rewriting it in the form

$$\theta = \frac{ap}{1 + ap}. \quad (29)$$

If the surface is covered to a small extent only, then $1 - \theta \approx 1$; hence, Eq. (28) reduces to

$$\theta = ap, \quad (30)$$

the extent of adsorption being proportional to the pressure.

Although Eqs. (29) and (30) were derived from (7), which was based on the assumption that each adsorbed molecule occupies only one center, a similar result would be obtained from Eq. (13), for the case of a gas molecule requiring two adjacent sites for adsorption.

Adsorption with Dissociation.—The application of quantum mechanics to the system consisting of a molecule of hydrogen and two surface atoms of carbon or nickel has led to the con-

clusion that in the most stable configuration the distance between the absorbed hydrogen atoms is much greater than in a normal molecule (see page 343). It follows, therefore, that in these instances adsorption is accompanied by dissociation of the adsorbed molecule. It is probable that many cases of activated adsorption involve dissociation, and hence it is necessary to consider what effect this will have on the equations for the rates of adsorption and desorption and on the adsorption isotherm. Two main types of behavior may be distinguished: (1) that in which the molecule undergoes dissociation in the course of adsorption but the atoms remain on adjacent sites; (2) that in which dissociation results from the jump of one or both of the atoms constituting the molecule from one site to another. In the first case the activated complex may be depicted as shown in Fig. 93; G_2 is the adsorbed gas molecule and S_2 represents the two adjacent sites. The equilibrium between initial, activated and final states may be written as

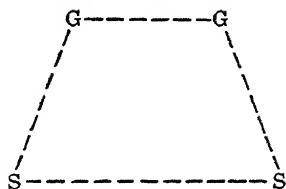
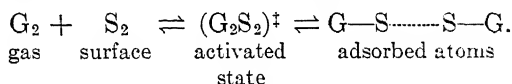


FIG. 93.—Activated state for adsorption of gas molecule (G_2) on two adjacent sites (S_2).



The rate of adsorption is given by an equation similar to (7) or by any of the succeeding equations that are equivalent to it, and that of desorption by one identical with Eq. (20) or (21); the adsorption isotherm will then be identical with Eqs. (27), (28) and (29).

When dissociation results from the jump of an atom from one site to another, two possibilities may arise: the actual adsorption of the molecule may be rapid and the jump of the atom slow, or the adsorption of the molecule may be the rate-determining stage. In the former case, the activated state may be considered to be as depicted in Fig. 94, so that the adsorption and desorption equilibrium can be represented as

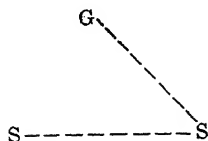
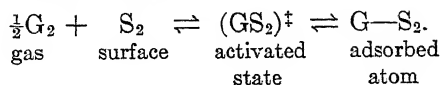


FIG. 94.—Activated state for jump of an atom (G) from one adsorption site to another.



The rate of adsorption can be readily shown, by the method used in deriving Eqs. (7), etc., to be given by

$$v_1 = c_g^{1/2} c_s \frac{kT}{h} \cdot \frac{f_{\pm}}{F_g^{1/2} f_s} e^{-\epsilon_1/kT}, \quad (31)$$

where the symbols have the same significance as previously. Similarly, the rate of desorption is

$$v_2 = c_a \frac{kT}{h} \cdot \frac{f_{\pm}}{f_a} e^{-\epsilon_2/kT}. \quad (32)$$

When equilibrium is attained, v_1 is equal to v_2 , hence

$$\frac{c_a}{c_s} = c_g^{1/2} \frac{f_a}{f_s F_g^{1/2}} e^{\epsilon/kT}. \quad (33)$$

If, as before, θ is the fraction of the surface covered, now by adsorbed atoms, it follows from Eq. (33), by the arguments used in deriving Eqs. (27) and (28), that²²

$$\frac{\theta}{1-\theta} = p^{1/2} \frac{h^{3/2}}{(2\pi)^{3/4} (kT)^{3/4}} \cdot \frac{b_a}{b_g^{1/2}} e^{\epsilon/kT}, \quad (34)$$

or

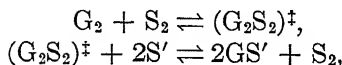
$$1 - \theta = ap^{1/2}; \quad (35)$$

$$\therefore \theta = \frac{ap^{1/2}}{1 + ap^{1/2}}. \quad (36)$$

At low pressures, or in general when the surface is sparsely covered,

$$\theta = ap^{1/2}. \quad (37)$$

In the second type of dissociation, when the adsorption of the molecule is rate-determining, the processes may be represented by



where S_2 is a dual site on which the molecule of G_2 is first adsorbed and S' represents a site to which each atom finally jumps. The over-all change is seen to be, as before, the adsorption of G_2 on two S' sites in the form of atoms. By considering the equilib-

²² Cf. Fowler, Ref. 20.

rium between initial and activated states, it is found that the rate of adsorption is given by

$$v_1 = c_g c_s \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g f_s} e^{-\epsilon_1/kT}, \quad (38)$$

where c_s is the concentration of dual sites. Similarly the rate of desorption is

$$= \frac{c_a c_s}{c_{s'}^2} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger} f_{s'}^2}{f_a^2 f_s} e^{-\epsilon_2/kT}, \quad (39)$$

where $c_{s'}$ is the concentration of single S' sites. By equating (38) and (39), the adsorption isotherm is seen to be

$$\frac{c_a}{c_{s'}} = c_g^{1/2} \frac{f_a}{f_s F_g^{1/2}} e^{\epsilon/kT}. \quad (40)$$

This equation is identical in form, as is necessary, with (33) and hence leads to equations of the same type as (34) to (37). However, the expressions for the rates of adsorption and desorption are different; thus, according to Eq. (31) the rate is proportional to the square root of the gas pressure, whereas according to (38) it is proportional to its first power. In most of the examples that have been studied the exponent is unity rather than one-half, so that the second mechanism, in which the adsorption of the molecule is rate-determining, appears to be the more common. That this is so is confirmed by the agreement between calculated and observed values for adsorption rates in Table XXXIX. Agreement was obtained by the use of Eq. (13), which is equivalent to Eq. (38), whereas if Eq. (31) had been used there would have been large discrepancies between the calculated and observed values. It may be noted in particular that the application of Eq. (31) to Roberts's data on the adsorption of hydrogen on tungsten (page 352) leads to rates which are faster than those derived from Eq. (13) and therefore still more in disagreement with the experimental values.

Adsorption with Interaction.—In the foregoing treatment the possibility of interaction between adsorbed molecules or atoms has been ignored, and this may account for the deviations frequently observed from the behavior to be expected from the adsorption isotherms given above. In particular, it has been

found that the variation of the constant a with temperature is in the opposite direction to that expected. Such deviations can be explained in two ways: (1) They may be due to interaction between the adsorbed particles. (2) The variability of the surface may be responsible. Both these factors probably play an important part in adsorption processes.

Allowance may be made in a number of ways for the interaction between adsorbed molecules; two of these will be considered. Before proceeding with the problem, however, it is necessary to understand clearly the difference between mobile and immobile surface layers.²³ A mobile layer is one in which the energy of activation necessary to enable a molecule to move from the site on which it is adsorbed to a neighboring unoccupied site is small in comparison with its thermal energy. The molecules will, therefore, move freely on the surface, and they will distribute themselves according to the Maxwell-Boltzmann statistics. Experimental evidence of the occurrence of this type of adsorption has been obtained in certain instances.²⁴ If, on the other hand, the activation energy required for movement from one site to another on the surface is much greater than the thermal energy of the adsorbed molecules, the latter will tend to remain at the positions on which they were originally adsorbed; the layer is then said to be immobile.

The treatment of mobile and immobile layers involves finding a solution of the problem of the distribution of adsorbed molecules on the surface, for any number of such molecules. An exact solution has not yet been developed; but the following approximate treatment, based on a special technique that was first used in the study of order-disorder phenomena in alloys, gives a good qualitative picture of the conditions on a surface.²⁵ Consider an immobile film, and suppose the adsorbed atoms are attached at definite positions on the surface, which may be

²³ Cf. J. K. Roberts, "Some Problems in Adsorption," Chap. II, Cambridge University Press, 1939.

²⁴ M. Volmer and G. Adhikari, *Z. physik. Chem.*, **119**, 46 (1926); *Z. Physik*, **35**, 170 (1925).

²⁵ R. Peierls, *Proc. Cambridge Phil. Soc.*, **32**, 471 (1936); J. K. Roberts, *Proc. Roy. Soc.*, **161**, A, 141 (1937); *Proc. Cambridge Phil. Soc.*, **34**, 399, 577 (1938); **36**, 53 (1940); see also I. Langmuir, *J. Chem. Soc.*, 511 (1940); L. Tonks, *J. Chem. Phys.*, **8**, 477 (1940).

represented by a quadratic lattice, as shown in Fig. 95. In order to simplify the problem, only interactions between particles that are near neighbors are considered; for example, the interactions between a and b and between b and c are included, but not those between a and c . It is supposed that there is a repulsion energy V between such near neighbors, and the corresponding Boltzmann term $e^{-V/kT}$ is represented by the symbol η . The energy of adsorption for an atom adsorbed on a site that is surrounded by empty sites is called ϵ .

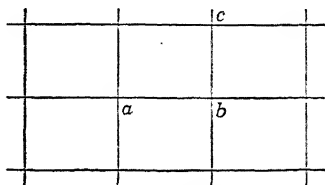


FIG. 95.—Surface represented as a quadratic lattice.

The partition function per molecule of gas, writing kT/p in place of the volume occupied v , is

$$f_g = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{kT}{p} b_g, \quad (41)$$

where b_g , as before, represents the vibrational and rotational term; similarly, for an adsorbed molecule that has no near neighbors,

$$f_a = b_a e^{-\epsilon/kT}, \quad (42)$$

there being no translational contribution on account of the immobility in the surface layer. If a function ξ is defined as the ratio of the partition functions in the adsorbed and free states, then it follows from Eq. (42) that

$$= \frac{b_a}{f_g} e^{-\epsilon/kT}. \quad (43)$$

Consider one particular point on the adsorbing surface, such as a in Fig. 95, which may or may not be occupied by a gas molecule. In order to obtain the partition function for the system consisting of this central site and its s near neighbors, four in the case of Fig. 95, it is necessary to include all the possibilities as far as the occupation of the $s + 1$ sites is involved.

Suppose, in the first place, that the central site is unoccupied; then the following possibilities arise, as far as the other sites are concerned.

1. The neighboring sites may all be empty, in which case the partition function will be unity.

2. One of the s neighboring sites may be occupied by a molecule; the quantity ξ then gives the partition function relative to a molecule in the gas phase, apart from the influence exerted by molecules on the remainder of the surface. To allow for this effect the factor ζ is introduced, and the partition function for the given configuration of the molecule on the site adjacent to the central one is $\xi\zeta$, which may be represented by Φ . The situation in which one neighboring site is occupied may, however, arise in s different ways; and so the partition function must be weighted by this factor, giving as a result ${}_1P\Phi$, where the symbol ${}_1P$ stands for the number of different ways in which one site can be chosen from a total of s possible sites.

3. Two of the neighboring sites may be occupied, in which case the partition function for each configuration is Φ^2 ; and since this situation may arise in ${}_2P$ different ways, the resulting partition function is ${}_2P\Phi^2$.

4. In the general case, if n sites adjacent to the central one are occupied, the partition function is ${}_nP\Phi^n$.

The total partition function for the case in which the central site is empty is, therefore, equal to the sum of $s + 1$ terms; *i.e.*,

$$f = 1 + {}_1P\Phi + {}_2P\Phi^2 + {}_3P\Phi^3 + \cdots + {}_sP\Phi^s + \cdots + {}_sI$$

$$= \sum_{n=0}^s {}_nP\Phi^n \quad (44)$$

$$= (1 + \Phi)^s. \quad (45)$$

It is necessary to consider next the case in which the central site is occupied; the various possibilities with regard to the surrounding positions are as follows:

1. The surrounding sites are all empty; in this case the partition function is ξ .

2. If one neighboring site is occupied, the partition function is $\xi^2\zeta\eta$, *i.e.*, $\xi\eta\Phi$, where η is the factor derived above that allows for the repulsive interaction between two neighboring molecules and ζ still refers to interaction by more distant molecules. Since there are s ways of choosing the occupied site, the factor ${}_1P$ must be employed to weight the partition function.

3. When two sites adjacent to the central one are occupied, the partition function is $\xi^3 \zeta^2 \eta^2$, *i.e.*, $\xi(\eta\Phi)^2$, and the weighting factor is ${}_2P$.

4. If n sites are occupied, the total partition function is ${}_nP\xi(\eta\Phi)^n$.

The sum of all these terms gives the total partition function for all the different possibilities: thus,

$$\begin{aligned} f &= \xi + {}_1P\xi(\eta\Phi) + {}_2P\xi(\eta\Phi)^2 \\ &\quad + \cdots + {}_nP\xi(\eta\Phi)^n + \cdots + {}_sP\xi(\eta\Phi)^s \quad (46) \\ &= \xi(1 + \eta\Phi)^s. \quad (47) \end{aligned}$$

The ratio of the partition functions (45) and (47) is clearly the ratio of the probability of the central site being empty to that of its being occupied, and this is equivalent to $(1 - \theta)/\theta$; it follows, therefore, that

$$\frac{\theta}{1 - \theta} = \xi \left(\frac{1 + \eta\Phi}{1 + \Phi} \right)^s. \quad (48)$$

Substituting for ξ the value given by Eqs. (41) and (43), the result is the adsorption isotherm

$$\frac{\theta}{1 - \theta} = p \frac{h^3}{(2\pi m)^{3/2} (kT)^{3/2}} \cdot \frac{b_a}{b_g} e^{e/kT} \left(\frac{1 + \eta\Phi}{1 + \Phi} \right)^s, \quad (49)$$

which differs from Eq. (27) by the inclusion of the interaction factor $[(1 + \eta\Phi)/(1 + \Phi)]^s$.

Simplified Treatment of Interaction Effects.—The introduction of interaction effects in this manner leads to somewhat unwieldy expressions, and it is useful to have a simpler treatment. In the study of binary solutions (*cf.* page 412), it is found that a very satisfactory approximation is to consider that the interaction terms make the most important contribution to the energy of the system and that the entropy remains almost unaffected. It is of interest, therefore, to apply the same approximation to the essentially similar problem of molecular interaction in an adsorbed film. Consider, in the first place, an immobile layer in which each molecule, as it exists in the gas phase, occupies one site on the surface. At each stage of the adsorption process the number of occupied sites adjacent to

any given site will be, on the average, θs , since θ is the fraction of the total surface that is covered with adsorbed molecules. The influence of the molecules occupying the θs sites will therefore be to diminish the heat evolved in the adsorption of a single molecule by an amount $s\theta V$, where V is, as before, the repulsive interaction energy. If ϵ is the heat evolved in the adsorption of a molecule of gas on the bare surface, then when a fraction θ of the surface is occupied,

$$\text{Heat of adsorption} = \epsilon - s\theta V, \quad (50)$$

so that the heat of adsorption on an immobile film should be a

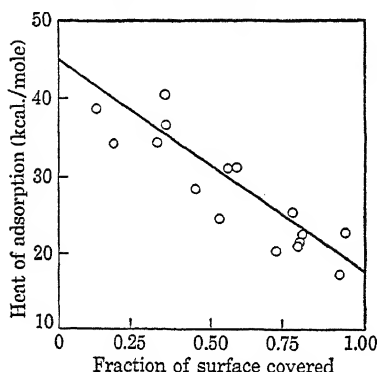


FIG. 96.—Heats of adsorption of hydrogen on tungsten. (Roberts.)

linear function of the fraction of surface covered. The heats of adsorption of hydrogen on clean tungsten for various proportions of covered surface have been measured by J. K. Roberts²⁶ whose data are plotted in Fig. 96; it is seen that the results approximate very closely to a straight line, and hence it appears that the hydrogen forms an immobile layer on a tungsten surface. The falling off in heat of adsorption

with increased extent of coverage is thus attributed to interaction between the adsorbed species.

It appears, therefore, that a possible method of allowing for interaction effects is to replace ϵ in Eq. (27) by $\epsilon - s\theta V$, instead of employing the interaction term involving η and Φ ; thus, the adsorption isotherm would be written

$$\frac{\theta}{1 - \theta} = p \frac{h^3}{(2\pi m)^{3/2} (kT)^{3/2}} \cdot \frac{b_a}{b_g} e^{(\epsilon - s\theta V)/kT}. \quad (51)$$

This more exact adsorption isotherm may be derived in the following alternative manner, which is analogous to the treatment adopted in the study of diffusion (page 530) and of electrode processes (page 575). Since, as seen above, the molecular inter-

²⁶ J. K. Roberts, Ref. 5.

action decreases the heat evolved in adsorption by an amount $s\theta V$, it is reasonable to suppose that the energy of activation for adsorption will be increased by a definite fraction α of this quantity. This represents the fraction of the repulsive force operative between the initial and activated states; any subsequent interaction effects will not influence the activation energy. The activation energy per molecule ϵ_1 for adsorption on a bare surface will thus be increased by an amount $\alpha s\theta V$, so that the total is $\epsilon_1 + \alpha s\theta V$. Molecular repulsions will, on the other hand, tend to diminish the activation energy for desorption by a fraction $1 - \alpha$ of the total interaction effect, and so the activation energy for this process becomes $\epsilon_2 - (1 - \alpha)s\theta V$. The rates of adsorption v_1 and desorption v_2 obtained by making the

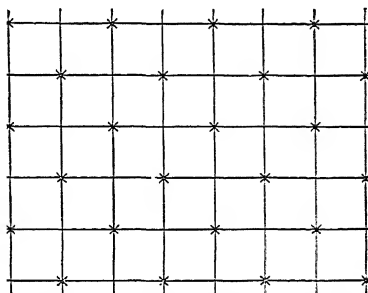


FIG. 97.—Quadratic lattice with no two adjacent positions occupied by adsorbed molecules.

appropriate alterations in the activation energies in Eqs. (8) and (21) are thus

$$v_1 = c_g c_s \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g f_s} e^{-(\epsilon_1 + \alpha s\theta V)/kT}, \quad (52)$$

and

$$v_2 = c_a \frac{kT}{h} \cdot \frac{f_{\ddagger}}{f_a} e^{[\epsilon_2 - (1 - \alpha)s\theta V]/kT}. \quad (53)$$

At equilibrium, when the two rates are equal, the ratio of covered to uncovered surface is given by the method used in deriving Eq. (27) as

$$\frac{\theta}{1 - \theta} = p \frac{h^3}{(2\pi m)^{3/2} (kT)^{3/2}} \cdot \frac{v_a}{v_g} e^{(\epsilon - s\theta V)/kT}, \quad (54)$$

where ϵ , as before, is equal to $\epsilon_2 - \epsilon_1$, the heat of adsorption

per molecule on a bare surface. This result is seen to be identical with Eq. (51).

It may be pointed out that the argument employed above involves the tacit assumption that for an immobile film the energy of activation, like the heat of adsorption, varies in a linear manner with the fraction of surface covered. If, on the other hand, the molecules in the adsorbed layer were mobile, they would tend to arrange themselves in the configuration of lowest energy, but this tendency would be opposed by thermal motion. For a surface such as is depicted in Fig. 95, however, the influence of this motion can be neglected in the first approximation. It is evident that up to $\theta = 0.5$ the molecules can

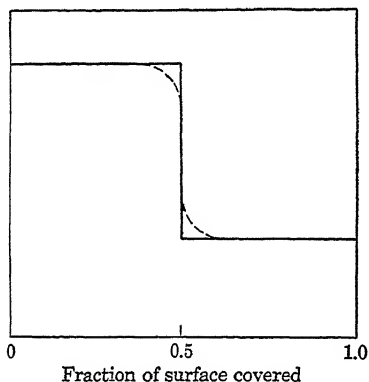


FIG. 98.—Variation of heat of adsorption with fraction of surface covered, allowing for molecular interaction.

arrange themselves in such a way (see Fig. 97) that no two are in adjacent positions; according to the approximation made above that all interactions except those between near neighbors may be ignored, the interaction energy will then be zero. When θ exceeds 0.5, however, interaction must play a part, since every molecule that is now adsorbed must find itself surrounded by four molecules, for the quadratic lattice shown in Fig. 97; the heat of adsorption, which has hitherto remained constant, should now fall to $\epsilon - 4V$ (Fig. 98). The effect of taking into account the thermal motion of the molecules and assuming a Maxwell-Boltzmann distribution of energy is to round off the corners (Fig. 98) to an extent depending on the value of V/kT .²⁷

Adsorption on a Covered Surface.—For certain purposes in connection with the problem of heterogeneous reactions (see page 382) it is desirable to consider adsorption of a gas on a surface already covered to a large extent by another substance, *e.g.*, a poison. In the simplest case the adsorption of gas and poison may be supposed to occur on the same sites, which may be dual or single; hence, Eq. (8) is applicable. If the adsorption

²⁷ J. S. Wang, *Proc. Roy. Soc.*, **161**, A, 127 (1937).

isotherm, Eq. (23), is written in the abbreviated form

$$\frac{c_a}{c_s} = A c_g, \quad (55)$$

where A is $(f_a/F_g f_s) e^{\epsilon_p/kT}$, then using the suffix p to indicate the poison, the corresponding isotherm for this substance is

$$\frac{c_{ap}}{c_s} = A_p c_{gp}, \quad (55a)$$

where A_p is $(f_{ap}/F_{gp} f_s) e^{\epsilon_p/kT}$. Let L be the total number of adsorption sites on 1 sq. cm. of bare surface. This is equal to $c_s + c_a + c_{ap}$; but if the poison covers the larger part of the surface, c_a may be neglected, so that L is approximately equal to $c_s + c_{ap}$. Upon substituting the value of c_{ap} given by Eq. (55a), it is seen that

$$c_s = \frac{L}{1 + A_p c_{gp}}; \quad (56)$$

hence, Eq. (8) for the rate of adsorption of gas becomes

$$v_1 = \frac{L c_g}{1 + A_p c_{gp}} \cdot \frac{kT}{h} \cdot \frac{f_+}{F_g f_s} e^{-\epsilon_1/kT}. \quad (57)$$

For a strongly adsorbed poison, unity may be neglected in comparison with $A_p c_{gp}$; and upon substituting the value for A_p given above,

$$v_1 = L \frac{c_g}{c_{gp}} \cdot \frac{kT}{h} \cdot \frac{f_+ F_{gp}}{f_{ap} F_g} e^{-(\epsilon_1 + \epsilon_p)/kT}. \quad (58)$$

The rate of adsorption is seen to vary as the pressure of the gas and inversely as the pressure of the strongly adsorbed poison, and the heat of activation for adsorption is increased from ϵ_1 to $\epsilon_1 + \epsilon_p$, where ϵ_p is the heat (evolved) of adsorption of the poison.

The influence of a strongly adsorbed poison on the activation energy for adsorption is immediately evident from the appropriate potential-energy diagram. If the surface is covered by a strongly adsorbed substance to a considerable extent, it is necessary for this to be desorbed before either the activated complex can form on the surface or the gas molecule be finally adsorbed. The potential-energy curve for adsorption on a

clean surface, represented by the full line in Fig. 99, is thus changed to the dotted line for adsorption on a covered surface. The potential energies of activated and final, *i.e.*, adsorbed, states are raised by an amount ϵ_p numerically equal to the heat of desorption (or adsorption) of the poison. It is apparent that the energy of activation for adsorption on the poisoned surface is $\epsilon_1 + \epsilon_p$, where ϵ_1 is the corresponding value for the clean surface. An examination of the curves shows, however, that the activation energy for desorption remains unchanged.

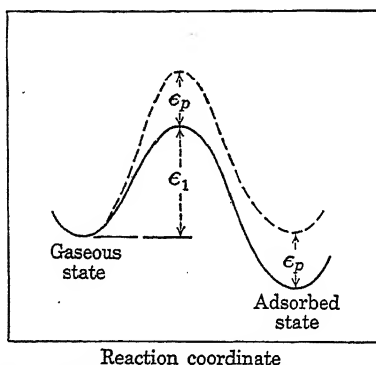


FIG. 99. -Potential-energy curve for adsorption on a poisoned surface.

It may be pointed out that the rate of adsorption is not decreased so much as might be supposed from the increase in the heat of activation, because the adsorption of a gas molecule is accompanied by the transfer of a poison molecule from the surface to the gas phase; there is, consequently, a gain of entropy compared with that for adsorption on a bare surface. It can be readily shown* that A_p is equal to $e^{-\Delta F_p^0/kT}$, where ΔF_p^0 is the standard free energy of adsorption per molecule of the poison; and upon writing Eq. (8) in the alternative form

$$v_1 = c_g c_s \frac{kT}{\tau} e^{-\Delta F_1^\ddagger/kT}, \quad (59)$$

where ΔF_1^\ddagger is the free energy of activation per molecule for adsorption on a bare surface, it follows from Eq. (58) that for a

* For any equilibrium $A + B \rightleftharpoons C$, the quantity $(F_C/F_A F_B) e^{-E_0/RT}$ is equal to the equilibrium constant and hence to $e^{-\Delta F^0/RT}$, where ΔF^0 is the standard free-energy change (*cf.* p. 188).

surface covered by a poison

$$v_1 = L \frac{c_g}{c_{gp}} \cdot \frac{kT}{z} e^{-(\Delta F_1^\ddagger - \Delta F_p^0)/kT} \quad (60)$$

In view of the large change of entropy accompanying adsorption and desorption (*cf.* page 397), ΔF_p^0 is often a small negative quantity; hence, $\Delta F_1^\ddagger - \Delta F_p^0$ may be little different from ΔF_1^\ddagger . For a strongly adsorbed poison, however, ΔF_p^0 will have a large negative value, and the rate of adsorption of the gas will be markedly decreased.

Since the activation energy for desorption is unaffected by the poison,* the rate of desorption of gas from a poisoned surface is still given by Eq. (21); and, from this and Eq. (58), it follows that the appropriate "isotherm" is

$$c_a = L \frac{c_g}{c_{gp}} \cdot \frac{F_{gp} f_a}{F_{ga} f_{ap}} e^{(\epsilon - \epsilon_p)/kT}, \quad (61)$$

where ϵ , as before, is $\epsilon_2 - \epsilon_1$ the heat (evolved) of adsorption per molecule of the gas on a bare surface. The effective heat of adsorption on the poisoned surface is, according to Eq. (61), equal to $\epsilon - \epsilon_p$, in agreement with Fig. 99; the heat evolved in adsorbing the gas is reduced by the amount required to desorb the poison.

By utilizing the methods developed in this section, equations analogous to (58) and (61) can be derived for various types of adsorption, *e.g.*, involving dual sites or dissociation, of both gas and poison. An illustration is provided later (page 384) by the treatment of the decomposition of ammonia, adsorbed on a dual site, on a surface poisoned by hydrogen in the form of atoms.

CHEMICAL REACTIONS ON SURFACES

The Rate-determining Step in Heterogeneous Reactions.—

From the standpoint of the theory of absolute reaction rates, it is sufficient to consider the equilibrium between initial and activated states only and to disregard all other aspects of the reaction.

* This would be strictly true only if in the activated state for desorption the molecule of poison is not involved. If the poison forms a bond with the surface while the adsorbed molecule is in the process of being desorbed, the activation energy for desorption would be decreased.

but it is frequently of interest to examine the mechanism of the process in more detail. A reaction occurring at a surface may, in general, be separated into five steps, the slowest of which will determine the rate of the over-all process. The successive stages are

1. Transport of the gaseous reactants to the surface.
2. Adsorption of the gases.
3. Reaction on the surface.
4. Desorption of the products.
5. Transport of the liberated products from the surface into the bulk gas phase.

Diffusion as the Rate-determining Step.—The stages 1 and 5 are ordinary diffusion processes, and if either of them were the rate-determining step the temperature coefficient of the rate would be of the same order as for gaseous diffusion. The rate of diffusion of a gas does not vary exponentially with the temperature, however, as do the rates of heterogeneous chemical reactions, but it increases in proportion to the square root of the temperature. Further, surface reactions generally have activation energies of the order of 30 kcal. (see Table XLIV, page 390), whereas for the diffusion processes the values are probably very small. The retarding influence of sulfur trioxide on the combination of sulfur dioxide and oxygen on a platinum surface was at one time attributed to the necessity for the reacting molecules to diffuse through a layer of trioxide before reaching the surface. If the rate of combination on the surface were rapid compared with diffusion, so that the latter represented the rate-determining step, the results could be explained. It has been pointed out,²⁸ however, that the layer of trioxide would have to be of visible dimensions in order to account quantitatively for the observed retardation. It is improbable, therefore, that diffusion to the surface is the slow stage in the reaction.

It may be noted that the rate of diffusion to and from the catalyst is often of importance in technical gas reactions when the circumstances are such that the velocity of gas flow is the factor determining the over-all rate at which the product is obtained. Diffusion is also frequently the rate-determining step in the case of solid-liquid reactions, owing to its relatively slow rate in solution.

²⁸ I. Langmuir, *J. Am. Chem. Soc.*, **38**, 1145 (1916).

Adsorption or Desorption as Rate-determining.—In general the process 2 or 4 may be expected to be the slow step in a heterogeneous reaction if the activation energy of adsorption or desorption is high or if the surface reaction 3 is rapid because of a low activation energy. Such a rapid reaction is generally to be expected if the adsorbed particles are atoms, the combination of which requires little or no activation energy. The high-temperature heterogeneous ortho-para hydrogen conversion²⁹ and the establishment of equilibrium between hydrogen and deuterium³⁰ are probably reactions in which desorption of the product is the rate-determining step. The mechanism suggested for the ortho-para conversion is the chemisorption of hydrogen on the surface of the catalyst, which involves dissociation into atoms, followed by a rearrangement of the latter to give equilibrium amounts of ortho- and para-molecules. This suggestion is supported by the observation³¹ that there is a parallelism between the activity of a surface in inducing the ortho-para conversion and its capacity for the activated adsorption of hydrogen. If the proposed mechanism is correct, it is very probable that the actual combination of the atoms on the surface will be rapid, and hence the slow stage in the reaction should be adsorption of the reactant or desorption of product. Adsorption or desorption is probably also the slow stage in the heterogeneous establishment of equilibrium between hydrogen and deuterium. The surface reaction presumably involves the combination of adsorbed atoms and so should require little activation energy. It is significant that the kinetics of the ortho-para hydrogen conversion process and of the hydrogen-deuterium reaction are very similar.

The catalytic production of ammonia from nitrogen and hydrogen, and the decomposition of ammonia, appear to involve adsorption and desorption, respectively, of nitrogen as the rate-determining step.³² It has been observed that isotopic exchange between deuterium and the hydrogen in ammonia

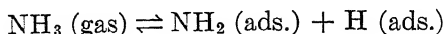
²⁹ K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **B**, *4*, 113 (1929); K. F. Bonhoeffer and A. Farkas, *ibid.*, **B**, *12*, 231 (1931).

³⁰ A. J. Gould, W. Bleakney and H. S. Taylor, *J. Chem. Phys.*, **2**, 362 (1934).

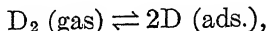
³¹ H. S. Taylor and A. Sherman, *J. Am. Chem. Soc.*, **53**, 1614 (1931); *Trans. Faraday Soc.*, **28**, 247 (1932).

³² H. S. Taylor and J. C. Jungers, *J. Am. Chem. Soc.*, **57**, 660 (1935).

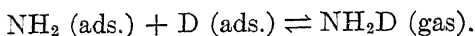
takes place even at ordinary temperatures on an active iron catalyst such as is used for the synthesis of ammonia. The exchange reaction probably involves activated adsorption of both the ammonia and the deuterium, accompanied by dissociation, thus,



and



followed by reassociation and desorption,



Adsorption of the NH_2D , dissociation into NHD and H and recombination with an adsorbed atom of D will result in the formation of NHD_2 ; finally, ND_3 can arise in an analogous manner. It is evident, therefore, that dissociation neither of hydrogen nor of ammonia can be the rate-determining stage in the synthesis or decomposition of ammonia, respectively, on active iron catalysts. By a process of elimination the conclusion is reached that the observed reaction rates must be attributed to the slowness of the activated adsorption and desorption of nitrogen. This view is supported by measurements on the velocity of activated adsorption of nitrogen by an iron catalyst;³³ if to the activation energy of adsorption derived from these data is added the heat of adsorption, the result, which is the activation energy of desorption, is 49 to 57 kcal. in the temperature region of 400°C. The observed activation energy for the decomposition of ammonia on an iron surface is about 54 kcal.,³⁴ which suggests that desorption of nitrogen is the rate-determining step in this reaction.

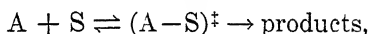
Theory of Absolute Reaction Rates.—The problem of a chemical reaction taking place on a surface is formally the same as adsorption, the initial state being a molecule, or molecules, in the gas phase and the activated state an adsorbed molecular species. The activated complex is, as usual, regarded as being in equilibrium with the initial reactants in the gas phase, so that the rate of reaction can be expressed in terms of the latter

³³ P. H. Emmett and S. Brunauer, *ibid.*, **55**, 1738 (1933); **56**, 35 (1934).

³⁴ E. Winter, *Z. physik. Chem.*, **B**, **13**, 401 (1931).

in the usual manner. Equations for the rates of surface reactions have been derived by I. Langmuir *et al.*,³⁵ from kinetic considerations; and it will be shown that analogous, but more explicit, equations may be obtained by using the method described in the earlier sections of this chapter of regarding the surface as one of the reactants. By means of these equations the rates of a number of heterogeneous gas reactions have been calculated and found to be in agreement with the experimental values. For present purposes, it is convenient to consider various reactions according to the number of molecules, *viz.*, one or two, involved in the chemical change.

Unimolecular Reactions.—Suppose the reaction involves one molecule of the gaseous reactant A, and S represents the active center on which reaction occurs. The activated complex consists of an adsorbed molecule which has acquired the appropriate amount of energy and the proper configuration; the equilibrium between initial and activated states may be written as



and hence, by the arguments used on page 347,

$$\frac{c_{\ddagger}}{c_g c_s} = \frac{f_{\ddagger}}{F_g f_s} e^{-\epsilon_0/kT},$$

where ϵ_0 is the energy of activation per molecule at 0°K. and the other symbols have the same significance as before. The rate of reaction according to the theory of absolute reaction rates is then

$$v = c_g c_s \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g f_s} e^{-\epsilon_0/kT}. \quad (62)$$

It may be noted that this expression is formally identical with Eq. (8) for the rate of adsorption; the activated states are, however, different in the two cases, although since both consist of immobile molecules attached to the surface their partition functions will be of the order of unity, in each case, at ordinary temperatures.

³⁵ I. Langmuir, *Trans. Faraday Soc.*, **17**, 621 (1922); C. N. Hinshelwood, "Kinetics of Chemical Change," p. 145, 1926, p. 187, 1940, Oxford University Press; H. S. Taylor, "Treatise on Physical Chemistry," p. 1074, D. Van Nostrand Company, Inc., 1931.

First-order Kinetics.—The application of Eq. (62) may be considered under two sets of conditions. In the first place, if the surface is sparsely covered by adsorbed molecules, c_s , the concentration of bare sites on the surface, is practically constant and is almost identical with the number of sites per square centimeter of completely bare surface. In these circumstances, c_s in Eq. (62) may be taken as constant, and the rate of reaction, for a given surface, is seen to be directly proportional to the concentration of the reacting material in the gas phase; the process is thus kinetically of the first order. Numerous examples of this type of behavior are known.

If the expressions for the partition functions are introduced into Eq. (62), it follows that the rate equation for a unimolecular, first-order reaction involving a diatomic molecule is

$$v = c_g c_s \frac{\sigma}{\sigma_{\ddagger}} \cdot \frac{\frac{1}{2} s h^4}{8\pi^2 I (2\pi m kT)^{3/2}} e^{-\epsilon_0/kT}, \quad (63)$$

where s is the total number of possible sites adjacent to any reaction center, σ and σ_{\ddagger} are the symmetry numbers of the molecules of reactant and of activated complex, respectively, and I and m are the moment of inertia and mass of the reacting molecule. For a nonlinear polyatomic molecule, the rate is

$$v = c_g c_s \frac{\sigma}{\sigma_{\ddagger}} \cdot \frac{\frac{1}{2} s h^5}{8\pi^2 (8\pi^3 ABC)^{1/2} (2\pi m)^{3/2} (kT)^{3/2}} e^{-\epsilon_0/kT}, \quad (64)$$

where A , B and C are the three moments of inertia of the reactant. In both these equations, c_s is the number of reaction sites per square centimeter of surface, and the factor $\frac{1}{2}s$ is introduced when the reacting molecules are attached to two sites in the activated state. By the use of known, or reasonable, values for the moments of inertia and taking s to be 4 in each case, the specific reaction rates for the surface decomposition of phosphine,³⁶ hydrogen iodide³⁷ and nitrous oxide³⁸ have been evaluated, the assumption being made that in each case the surface is smooth and sparsely covered, so that there are about 10^{15} individual sites

³⁶ J. H. van't Hoff and D. M. Kooij, *Z. physik. Chem.*, **12**, 155 (1893); cf. Temkin, Ref. 13.

³⁷ C. N. Hinshelwood and R. E. Burk, *J. Chem. Soc.*, **127**, 2896 (1925).

³⁸ C. N. Hinshelwood and C. R. Prichard, *Proc. Roy. Soc.*, **108**, A, 211 (1925).

per square centimeter. In Table XLI the calculated results are compared with those observed for relatively even surfaces; the values given are the ordinary first-order rate constants which refer to the particular amount of surface used in the experiment. Although the calculated and observed rates are in satisfactory agreement, it will be noted that the former are somewhat too small for the decomposition of phosphine and nitrous oxide. This may be due partly to the roughness of the surface, which would make the number of reaction centers greater than the value employed, and partly to the fact that there is some

TABLE XLI.—OBSERVED AND CALCULATED FIRST-ORDER SURFACE REACTION RATES

Decomposition of	Surface	T, °K.	Specific reaction rate, sec. ⁻¹	
			Calc.	Obs.
PH ₃	Glass	684	2.2×10^{-5}	4.7×10^{-7}
HI	Platinum	836	1.2×10^{-3}	1.0×10^{-1}
N ₂ O	Gold	1211	3.4×10^{-6}	12.3×10^{-5}

freedom of movement in the activated state. By taking the partition function for the latter to be unity, it is assumed that there is no movement of any kind in the activated state; with relatively complex molecules such as phosphine and nitrous oxide, rotation or libration in the activated state may well be appreciable, and the inclusion of the appropriate contribution to the partition function would increase the calculated reaction rates.

Zero-order Kinetics.—When the surface is covered by adsorbed molecules to an appreciable extent, the value of c_s varies with the pressure of the gas, and the behavior to be expected is apparent from a combination of Eq. (62) and the adsorption isotherm; upon substituting the following value for $c_g c_s$ obtained from Eq. (23), viz.,

$$c_g c_s = c_a \frac{F_a f_s}{f_a} e^{-\epsilon/kT}, \quad (65)$$

in (62), it follows that

$$v = c_a \frac{kT}{h} \cdot \frac{f_+}{f_a} e^{-(\epsilon_0 + \epsilon)/kT}, \quad (66)$$

where ϵ is the heat evolved in the adsorption of one molecule of reactant. If the surface is almost completely covered by adsorbed molecules, c_a may be taken as constant, and the rate of reaction as given by Eq. (66) is seen to be virtually independent of the pressure of the reactant; the process is then said to obey zero-order kinetics. It will be apparent that Eq. (66) treats the reaction from the standpoint of adsorbed molecules, instead of gas molecules, as the initial reactant; the "surface activation energy," *i.e.*, the difference in energy between the activated

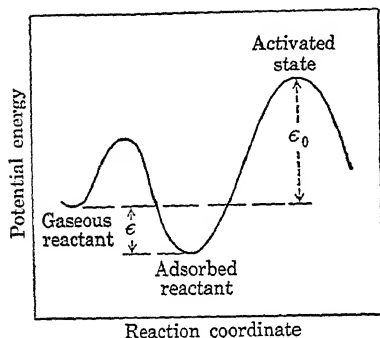


FIG. 100.—Potential-energy curve illustrating the "surface activation energy."

state and the *adsorbed* reactants, is $\epsilon_0 + \epsilon$. The same conclusion can be reached from an examination of the potential-energy curve for the surface reaction shown in Fig. 100. The difference in energy between the activated state and the initial gaseous reactant, which is equivalent to the experimental activation energy, is ϵ_0 per mole. The heat of adsorption of the reactant is ϵ , and hence it is

seen that the energy which an *adsorbed* molecule must acquire before it can pass over the energy barrier and react is $\epsilon_0 + \epsilon$.^{*39}

Since both f_{\ddagger} and f_a may be taken as unity, it follows that Eq. (66) may be written as

$$v = c_a \frac{kT}{h} e^{-E/RT} \quad (67)$$

where E is the observed activation energy per mole. An equation of the same form as (67), with a frequency factor assumed to be 10^{12} per second, in place of kT/h , was proposed from general considerations by B. Topley.⁴⁰

* The quantity that is here called the "surface activation energy" has sometimes been referred to as the "true activation energy," and ϵ_0 has been called the "apparent activation energy"; the latter terms are, however, misleading and will not be employed here.

³⁹ Cf. C. N. Hinshelwood and B. Topley, *J. Chem. Soc.*, **123**, 1014 (1923); Hinshelwood, *Ref. 35*, 1940.

⁴⁰ B. Topley, *Nature*, **128**, 115 (1931).

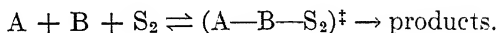
When the surface is almost entirely covered, c_a is equal to the number of activated centers per square centimeter of surface, which may be taken as 10^{15} . In Table XLII are given a number

TABLE XLII.—OBSERVED AND CALCULATED ZERO-ORDER SURFACE REACTION RATES

Decomposition of	Surface	E , kcal.	T , °K.	Specific reaction rates	
				Calc.	Obs.
NH_3^{41}	W	38	904	8.0×10^{15}	4×10^{17}
NH_3^{42}	W	41.5	1316	3.4×10^{21}	2×10^{19}
NH_3^{43}	Mo	53.2	1228	8.5×10^{15}	5 to 20×10^{15}
HI^{44}	Au	25.0	978	1.6×10^{17}	5.2×10^{22}

of calculated and observed rate constants, expressed as molecules per square centimeter per second, for zero-order reactions calculated from Eq. (67), making use of the data collected by Topley. The agreement is seen to be satisfactory except for the decomposition of hydrogen iodide on gold; the discrepancy may be due to the adsorption of hydrogen on the surface, for this would have the effect, as explained later, of increasing the activation energy and so would make the calculated reaction rate too low.

Bimolecular Reactions.—In a surface reaction between two molecules, it is presumably necessary that the molecules shall be adsorbed on adjacent sites. The reaction may thus be considered as occurring between one molecule of each of the reactants A and B and a dual site S_2 on the surface of the catalyst, thus,



It is first required to determine the number of dual sites in terms of the number of available single sites per square centimeter (c_s) and other factors. If the fraction of the surface covered by reactant A is θ and that covered by B is θ' , then the number of bare sites adjacent to any given site will be $s(1 - \theta - \theta')$, where s , as before, is the total number of possible

⁴¹ C. N. Hinshelwood and R. E. Burk, *J. Chem. Soc.*, **127**, 1051 (1925).

⁴² C. H. Kunsman, E. S. Lamar and W. E. Deming, *Phil. Mag.*, **10**, 1015 (1930).

⁴³ R. E. Burk, *Proc. Nat. Acad. Sci.*, **13**, 67 (1927).

⁴⁴ C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 1552 (1925).

sites adjacent to any given site. The number of dual sites per square centimeter is thus $\frac{1}{2}c_s s(1 - \theta - \theta')$, the factor $\frac{1}{2}$ arising from the fact that in the foregoing each dual site is counted twice. The fractions θ and θ' may be expressed in terms of the concentrations of adsorbed molecules, or atoms, of A, *i.e.*, c_a , and of B, *i.e.*, $c_{a'}$, as follows,

$$\theta = \frac{c_a}{c_a + c_{a'} + c_s} \quad (68)$$

and

$$\theta' = \frac{c_{a'}}{c_a + c_{a'} + c_s} \quad (69)$$

and so the number of dual sites per square centimeter may be written in the form

$$\text{Concentration of dual sites} = \frac{\frac{1}{2}sc_s^2}{L}, \quad (70)$$

where L stands for $c_a + c_{a'} + c_s$, the total number of sites per square centimeter of bare surface. The theory of absolute reaction rates then gives the velocity of the bimolecular surface reaction as

$$v = \frac{1}{2}s \frac{c_g c_{g'}}{L} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g F_{g'} f_s} e^{-\epsilon_0/kT}, \quad (71)$$

where c_g and $c_{g'}$ are the concentrations of A and B in the gas phase, F_g and $F_{g'}$ are their partition functions for unit volume and f_{\ddagger} and f_s are the partition functions for activated complex and for the reaction sites, respectively. Since L is the sum of c_a , $c_{a'}$ and c_s , it is possible to express Eq. (71) in terms of c_g , $c_{g'}$ and c_s by substituting the appropriate values of c_a and $c_{a'}$ given by the adsorption isotherm, Eq. (65). It is convenient, in this connection, to consider a number of special cases.

1. *Sparsely Covered Surface*.—When the surface is sparsely covered, *i.e.*, when the sum of c_a and $c_{a'}$ is small, L is practically equal to c_s , and hence Eq. (71) becomes

$$v = \frac{1}{2}sc_g c_{g'} \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g F_{g'} f_s} e^{-\epsilon_0/kT}. \quad (72)$$

This represents the simplest type of second-order kinetics, the rate of the heterogeneous reaction being directly proportional to the concentration of each of the reactants: provided that c_s is

known, *e.g.*, for a smooth sparsely covered surface, it is possible to calculate the reaction rate from Eq. (72).

The velocity of the reaction between nitric oxide and oxygen on a glass surface has been measured at 85°K. and found to be represented by the expression

$$v = 9.4 \times 10^{-27} c_{\text{NO}} c_{\text{O}_2} e^{-\epsilon_0/kT} \text{ molecules cm.}^{-2} \text{ sec.}^{-1}$$

with concentrations of the reacting gases in molecules per cubic centimeter.⁴⁵ In this equation, ϵ_0 is the activation energy at 0°K., a slight adjustment having been made, by means of the theoretical equation (72), to the experimental activation energy observed at 85°K. (*cf.* page 195). The dependence of the rate on the product of the concentrations of the reactants suggests that the activated complex consists of a molecule of NO and one of O₂ adsorbed on neighboring sites on the surface, so that Eq. (72) should be applicable. The ratio of the partition functions for the adsorbed, immobile, activated complex and for the adsorption centers, *i.e.*, f_{\ddagger}/f_s , may be taken as unity, and F_{NO} and F_{O_2} may be calculated in the usual manner for diatomic molecules, the vibrational contributions being very little different from unity at the experimental temperature. Both nitric oxide and oxygen have multiplet ground states (*cf.* page 178), and allowance should be made for these in deriving the partition functions; but since the electron multiplicity of the activated complex is unknown, it may be assumed that the values cancel each other; this approximation cannot be in error by a factor of more than 2 or 3. Since the experimental results suggest a sparsely covered surface, the number of individual reaction sites, c_s , is about 10¹⁵ per square centimeter. If every site is surrounded by four others, *i.e.*, s is 4, and if two adjacent sites are involved, it is found from Eq. (72) that

$$v = 14.8 \times 10^{-27} c_{\text{NO}} c_{\text{O}_2} e^{-\epsilon_0/kT} \text{ molecules cm.}^{-2} \text{ sec.}^{-1},$$

in good agreement with the experimental result.

2. *One Reactant More Strongly Adsorbed than the Other.*—If the reactant A is more strongly adsorbed than B, then c_a' may be neglected in comparison with c_a , and L may be put equal to $c_a + c_s$; Eq. (71) then becomes

$$v = \frac{1}{2}s \frac{c_g c_a' c_s^2}{c_a + c_s} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g F_g f_s} e^{-\epsilon_0/kT}. \quad (73)$$

⁴⁵ M. Temkin and W. Pyzhov, *Acta Physicochim. U.R.S.S.*, **2**, 473 (1935).

Upon writing the adsorption isotherm, as on page 367, in the abbreviated form $c_a/c_s = Ac_g$, where A is equal to $(f_a/F_g f_s) e^{\epsilon/kT}$, and using this relationship to eliminate c_a from Eq. (73), it is found that

$$v = \frac{1}{2}s \frac{c_g c_{g'} c_s}{1 + Ac_g} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g F_g' f_s} e^{-\epsilon_0/kT}. \quad (74)$$

Further, since L is approximately equal to $c_a + c_s$, as already seen, it follows [cf. Eq. (56)] that $c_s = L/(1 + Ac_g)$; and substitution for c_s in Eq. (74) gives

$$v = \frac{1}{2}s \frac{L c_g c_{g'}}{(1 + Ac_g)^2} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g F_g' f_s} e^{-\epsilon_0/kT}, \quad (75)$$

which is equivalent to the more familiar form

$$v = \frac{k' p_A p_B}{(1 + B p_A)^2}, \quad (76)$$

where k' and B are constants at a definite temperature. It is of interest to note that if $c_{g'}$ or p_B is kept constant as c_a or p_A is increased the reaction velocity should pass through a maximum; behavior of this kind has been observed in the reaction between hydrogen and carbon dioxide on platinum.⁴⁶

3. *One Reactant Very Strongly Adsorbed.*—If the reactant A is so strongly adsorbed that it occupies most of the available surface, the fraction c_a/c_s , which is equal to Ac_g , is much greater than unity; in Eq. (75), therefore, unity may be neglected in comparison with Ac_g , and hence

$$v = \frac{1}{2}s \frac{L}{A^2} \cdot \frac{c_{g'}}{c_g} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g F_g' f_s} e^{-\epsilon_0/kT}. \quad (77)$$

If A is expressed as $(f_a/F_g f_s) e^{\epsilon/kT}$, Eq. (77) becomes

$$v = \frac{1}{2}sL \frac{c_{g'}}{c_g} \cdot \frac{kT}{h} \cdot \frac{F_g f_{\ddagger} f_s}{F_g' f_a} e^{-\epsilon_0'/kT}, \quad (78)$$

where ϵ_0' is equal to $\epsilon_0 + 2\epsilon$. The experimental activation energy will thus be greater by 2ϵ than the value for a sparsely covered surface of the same material. The reason for this increase is that two molecules of A must be desorbed before the activated complex can be formed. Equation (78) is equivalent to the expression

⁴⁶ C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 806 (1925).

derived by the method of Langmuir, $v = k'p_B/p_A$, where p_A and p_B are the partial pressures of the reactants A and B, which are proportional to c_g and c_g' , respectively. Several instances of this type of kinetics have been reported.⁴⁷

Equation (78) may be applied quantitatively to the reaction between carbon monoxide and oxygen on the surface of platinum. At 572°K. the observed rate⁴⁸ is equal to

$$v_{\text{obs.}} = 7.10 \times 10^{14} \frac{c_{\text{O}_2}}{c_{\text{CO}}} \text{ molecules cm.}^{-2} \text{ sec.}^{-1}$$

The temperature coefficient corresponds to an activation energy of 33.3 kcal. in this temperature region; the use of this value in Eq. (78) gives the calculated rate as

$$v_{\text{calc.}} = 4.33 \times 10^{15} \frac{c_{\text{O}_2}}{c_{\text{CO}}} \text{ molecules cm.}^{-2} \text{ sec.}^{-1},$$

in satisfactory agreement with experiment. The reaction between hydrogen and oxygen on platinum shows a similar behavior, but the data are not sufficiently precise to permit an application of the theory.

Bimolecular Reaction with a Single Reactant.—When both reacting molecules are the same, it can be readily seen that the general equation (71) simplifies to the form

$$v = \frac{1}{2}s \frac{c_g^2 c_s^2}{L} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g^2 f_s} e^{-\epsilon_0/kT}, \quad (79)$$

where L is equal to $c_s + c_a$. If the surface is sparsely covered, $L \approx c_s$, Eq. (79) reduces to

$$v = \frac{1}{2}s c_g^2 c_s \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g^2 f_s} e^{-\epsilon_0/kT}, \quad (80)$$

and the reaction behaves kinetically as a straightforward second-order process. At the other extreme, when the surface is almost completely covered, L is approximately equal to c_a , and hence $L = A c_g c_s$; insertion of L/A for $c_g c_s$ in Eq. (79) then gives

$$v = \frac{1}{2}s \frac{L}{A^2} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g^2 f_s} e^{-\epsilon_0/kT}. \quad (81)$$

⁴⁷ For example, see G.-M. Schwab, "Catalysis," (translated by H. S. Taylor and R. Spence), p. 227, D. Van Nostrand Company, Inc., 1937; Hinshelwood, Ref. 35, 1940.

⁴⁸ Langmuir, Ref. 35.

The reaction is clearly of zero order, since it is independent of the concentration, or pressure, of the reacting gas. Alternatively, if L is replaced by c_a , then

$$v = \frac{1}{2}s \frac{c_a}{A^2} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g^2 f_s} e^{-\epsilon_0/kT}. \quad (82)$$

In this equation, as in (66), the reaction is treated from the standpoint of the adsorbed molecules; if the value of A , given above, is inserted in Eq. (82), the result is

$$v = \frac{1}{2}sc_a \frac{kT}{h} \cdot \frac{f_{\ddagger}f_s}{f_a^2} e^{-(\epsilon_0+2\epsilon)/kT}, \quad (83)$$

which may be compared with Eq. (66) for a unimolecular reaction. In the present case, c_a is also constant, since the surface is almost fully covered, and the velocity of the reaction is independent of the pressure of the reactant, as already recorded. The surface activation energy is seen from Eq. (83) to be $\epsilon_0 + 2\epsilon$; the same conclusion may be reached from the potential-energy curve in Fig. 100, it being remembered that two adsorbed molecules are involved in the reaction.

Retardation by Poisons. 1. *Unimolecular Reactions.*—When the product of a reaction or another substance, *e.g.*, a poison, which may be present in the system, is strongly adsorbed, the process is retarded. For a unimolecular reaction occurring on a single site, the problem is similar to adsorption on a covered surface, considered on page 366. An equation exactly analogous to (57) is applicable, except that f_{\ddagger} is the partition function for the activated state and ϵ_1 is the heat of activation for the reaction; the rate equation may then be written in the more familiar form

$$v = \frac{k'p_A}{1 + Bp_P}, \quad (84)$$

where p_P is the partial pressure of the poisoning substance. If the poison is very strongly adsorbed and virtually covers the whole surface, this becomes

$$v = k' \frac{p_A}{p_P} \quad (85)$$

For such a surface an equation similar to (58) is applicable, the exponential term being $e^{-(\epsilon_0+\epsilon_P)}$, where ϵ_0 is the heat of

activation for the reaction on a clean surface and ϵ_p is the heat of adsorption of the product or poison. The experimental activation energy ($\epsilon_{\text{exp.}}$), the gas being considered as the reactant, is thus equal to $\epsilon_0 + \epsilon_p$. By utilizing the adsorption isotherm, equations (55) and (55a), together with the appropriate form of equation (58), and putting L equal to c_{ap} , since the surface is almost completely covered by poison, the rate equation takes the form

$$v = c_i \frac{kT}{h} \cdot \frac{f_{\ddagger}}{f_a} e^{-(\epsilon_0 + \epsilon)/kT}, \quad (86)$$

where ϵ is the heat of adsorption of the reactant. This equation again considers the reaction from the standpoint of adsorbed molecules of reactant, and the surface activation energy is seen to be $\epsilon_0 + \epsilon$, which is equal to $\epsilon_{\text{exp.}} + \epsilon - \epsilon_p$.

The potential-energy curve for reaction on a poisoned surface is shown by the dotted line in Fig. 101, which may be compared with the full line for the same process on a relatively bare surface. As in the case of Fig. 99 the former curve is raised on account of the necessity of desorbing the poison before either the reactants or the activated complex can be adsorbed.

The values of the surface activation energy and of the experimental activation energy for the poisoned surface are seen to be in agreement with those given above. If the substance which is strongly adsorbed on the reaction sites could be continuously removed, the experimental activation energy should diminish. This expectation is in agreement with the results obtained in the decomposition of alcohols on bauxite both in the presence and in the absence of water. When the latter, which is a reaction product that is strongly adsorbed by the catalyst, is continuously removed, the activation energy is reduced by 13 to 16 kcal.; this amount is comparable with the heat of adsorption (or desorption) of water vapor. Results of a similar kind have been obtained in other cases.

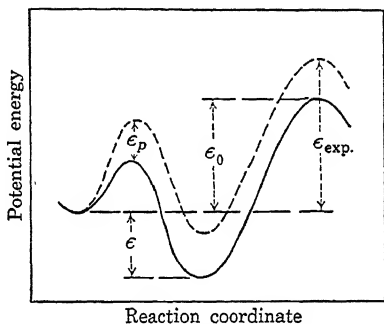


FIG. 101.—Potential-energy curves for reaction on clean and poisoned surfaces.

In Eq. (62) the quantity c_s represents the concentration of reaction centers, irrespective of whether they are single or dual sites; for the present purpose, however, it is necessary to restrict c_s to the concentration of single sites, and then the concentration of dual sites is given by Eq. (70). When this value is inserted in Eq. (62), the rate of a unimolecular reaction on dual sites becomes

$$v = \frac{1}{2}s \frac{c_g c_s^2}{L} \cdot \frac{kT}{h} \cdot \frac{f_+}{F_g f_s} e^{-\epsilon_0/kT}. \quad (87)$$

If the surface is almost completely covered by a reaction product or other substance acting as a poison, then L can be replaced by c_{ap} , the surface concentration of poison, which may be adsorbed either as molecules or as atoms. Since the latter case is of experimental interest, it alone will be considered; according to Eq. (33),

$$\frac{c_{ap}}{c_s} = c_{gp}^{1/2} \frac{f_{ap}}{f_s F_{gp}^{1/2}} e^{\epsilon_p/kT}; \quad (88)$$

hence, Eq. (87) may be written

$$v = \frac{1}{2}sL \frac{c_g}{c_{gp}} \cdot \frac{kT}{h} \cdot \frac{F_{gp} f_+ f_s}{F_g f_{ap}^2} e^{-(\epsilon_0 + 2\epsilon_p)/kT} \quad (89)$$

$$= k' \frac{p_A}{p_P}, \quad (90)$$

where c_g and c_{gp} are the concentrations of reactant and poison, respectively, in the gas phase and p_A and p_P are their partial pressures. The experimental heat of activation is seen to be $\epsilon_0 + 2\epsilon_p$; two atoms of poison must be desorbed in order that a dual site may be available for the reactant.

The rate of decomposition of ammonia at low pressures on a platinum surface varies as the pressure of the reactant and inversely as that of hydrogen, which acts as a poison; both Eqs. (85) and (90) satisfy these conditions, but the latter is probably applicable, since hydrogen is adsorbed atomically on platinum at high temperatures. It should, therefore, be possible to calculate the rate of reaction by means of Eq. (89). According to the experiments of G.-M. Schwab and H. Schmidt⁴⁹ the observed rate at 1423°K. is

$$v_{\text{obs.}} = 2.60 \times 10^{22} \frac{c_{\text{NH}_3}}{c_{\text{H}_2}} \text{ molecules cm.}^{-2} \text{ sec.}^{-1},$$

⁴⁹ G.-M. Schwab and H. Schmidt, *Z. physik. Chem.*, **B**, **3**, 337 (1929).

and the energy of activation is 44.3 kcal.* By taking this value as equivalent to $\epsilon_0 + 2\epsilon_p$ and considering f_{\ddagger} , f_s and f_{ap} to be unity, as usual, the rate of reaction for a smooth surface ($L = 10^{15}$ per square centimeter, $s = 4$) is calculated from Eq. (89) to be

$$v_{\text{calc.}} = 0.92 \times 10^{22} \frac{c_{\text{NH}_3}}{c_{\text{H}_2}} \text{ molecules cm.}^{-2} \text{ sec.}^{-1}$$

at 1423°K. Equally good agreement can, of course, be obtained at other temperatures, since the experimental activation energy is employed in the calculations.

2. *Bimolecular Reactions.*—If two molecules of a single reactant are involved, Eq. (79) is still applicable, but L is equal to $c_s + c_a + c_{ap}$. If the poison is fairly strongly adsorbed, c_a may be neglected in comparison with c_{ap} , and so L will be given by $c_s + c_{ap}$. When this value is inserted in Eq. (79), it is seen that

$$v = \frac{1}{2}s \frac{c_g^2 c_s^2}{c_s + c_{ap}} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g^2 f_s} e^{-\epsilon_0/kT}. \quad (91)$$

Upon substituting the value $A_p c_s c_{gp}$ for c_{ap} , Eq. (91) becomes

$$v = \frac{1}{2}s \frac{c_g^2 c_s}{1 + A_p c_{gp}} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g^2 f_s} e^{-\epsilon_0/kT}. \quad (92)$$

If the relationship $c_s = L/(1 + A_p c_{gp})$, i.e., Eq. (56), is utilized, it follows that

$$v = \frac{1}{2}s \frac{L c_g^2}{(1 + A_p c_{gp})^2} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g^2 f_s} e^{-\epsilon_0/kT}, \quad (93)$$

or

$$v = k' \frac{p_A^2}{(1 + B p_P)^2}, \quad (94)$$

where p_A and p_P are the pressures of reactant and poison, respectively, the latter being preferentially adsorbed.

* The figure 140 kcal. given by C. N. Hinshelwood and R. E. Burk [*J. Chem. Soc.*, **127**, 1114 (1925)] appears to apply at higher pressures when the reaction kinetics are more complicated, as found by G.-M. Schwab and H. Schmidt [*Z. physik. Chem.*, **B**, **3**, 337 (1929)]. The high temperature coefficient obtained under these conditions may be due to the operation of a chain reaction [cf. G.-M. Schwab, "Catalysis" (translated by H. S. Taylor and R. Spence), p. 316, 1937].

If the product is very strongly adsorbed, so that c_s can be neglected in comparison with c_{ap} , L becomes virtually equal to c_{ap} ; it is then found that

$$v = \frac{1}{2}s \frac{L}{A_p^2} \cdot \frac{c_g^2}{c_{gp}} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g^2 f_s} e^{-\epsilon_0/kT} \quad (95)$$

where A_p is $(f_{ap}/F_{gp}f_s) e^{\epsilon_p/kT}$. The same result may, of course, be obtained from Eq. (93) by neglecting unity in comparison with $A_p c_{gp}$, since A_p will be large for a strongly adsorbed substance. The general form of this equation is equivalent to $v = k' p_A^2 / p_P^2$, where A denotes the reacting substance and P the retarding material; the latter retards a bimolecular reaction according to the second power of its pressure, and not to the first, as has frequently been assumed. However, if the retarding gas is composed of diatomic molecules which are adsorbed in the form of atoms the equation takes the form

$$v = \frac{1}{2}s \frac{L}{A_p^2} \cdot \frac{c_g^2}{c_{gp}} \cdot \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_g^2 f_s} e^{-\epsilon_0/kT}, \quad (96)$$

where A_p has the value $(f_{ap}/F_{gp}^{1/2}f_s) e^{\epsilon_p/kT}$. The reaction rate now varies inversely as the first power of the pressure of the poison. The quantity A_p^{-2} , which appears in both Eqs. (95) and (96), involves $e^{-2\epsilon_p}$; and so the heat of activation is in each case $\epsilon_0 + 2\epsilon_p$, where ϵ_p is the heat of adsorption of a molecule of poison in the former case and of an atom in the latter.

Behavior of the type represented by Eq. (96) has been recorded for the decomposition of nitric oxide on platinum and on a platinum-rhodium alloy surface, which is retarded by oxygen.⁵⁰ At 1483°K. on pure platinum the rate is given as

$$v_{\text{obs.}} = 2.2 \times 10^{-4} \frac{c_{\text{NO}}^2}{c_{\text{O}_2}} \text{ molecules cm.}^{-2} \text{ sec.}^{-1}$$

Since the oxygen is adsorbed atomically on platinum, Eq. (96) should be applicable. Upon assuming f_{\ddagger} , f_s and f_{ap} to be unity and taking the activation energy to be 14 kcal.,⁵¹ the calculated rate is found to be

$$v_{\text{calc.}} = 2.9 \times 10^{-4} \frac{c_{\text{NO}}^2}{c_{\text{O}_2}} \text{ molecules cm.}^{-2} \text{ sec.}^{-1},$$

in excellent agreement with experiment.

⁵⁰ P. W. Bachman and G. B. Taylor, *J. Phys. Chem.*, **33**, 447 (1929).

⁵¹ G. E. Green and C. N. Hinshelwood, *J. Chem. Soc.*, 1709 (1926).

Similar equations may be deduced for the cases in which the two reacting molecules are different; these are analogous to Eqs. (93) and (94), except that $c_g c_{g'}$ replaces c_g^2 , where c_g and $c_{g'}$ are the concentrations of the two reacting gases, and $F_g F_{g'}$ is used instead of F_g^2 . No cases appear to be known in which equations of the resulting type are applicable, but the reaction between sulfur dioxide and oxygen on platinum is the nearest approach. The product, *i.e.*, sulfur trioxide, undoubtedly retards the reaction, but the reaction rate is not inversely proportional to the square of its pressure; the reaction is probably too complicated for the simple treatment given above to be applicable.

Dissociation of Hydrogen on Tungsten.—When a tungsten filament is heated in an atmosphere of hydrogen, the latter is converted into the atomic form which evaporates off from the surface of the tungsten and is generally adsorbed by the glass walls of the reaction vessel.⁵² The rate of formation of atomic hydrogen has been found, over a range of temperature (1148 to 1420°K.) and pressure (3×10^{-3} to 3.7×10^{-2} mm. of mercury), to be proportional to the square root of the pressure.⁵³ This result indicates clearly that the activated complex of the reaction consists of hydrogen atoms, not molecules (*cf.* page 359); hence, the rate equation should be

$$v = c_{\text{H}_2}^{1/2} c_s \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_{\text{H}_2}^{1/2} f_s} e^{-\epsilon_0/kT}. \quad (97)$$

The partition functions of the activated state and of the reaction centers on the surface may both be taken as unity; for even if the former consisted of a free hydrogen atom, it would be hemmed in by its neighbors and so have no freedom of movement. The vibrational partition function of molecular hydrogen is also virtually unity; Eq. (97) may thus be written in the form

$$v = c_{\text{H}_2}^{1/2} c_s \frac{kT}{h} \cdot \frac{1}{\left[\frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{8\pi^2 I kT}{2h^2} \right]^{1/2}} e^{-E_0/RT}. \quad (98)$$

The mechanism of the formation of atomic hydrogen on a tungsten surface appears to be the adsorption of a molecule;

⁵² I. Langmuir, *J. Am. Chem. Soc.*, **34**, 1310 (1912); **37**, 417 (1915).

⁵³ G. Bryce, *Proc. Cambridge Phil. Soc.*, **32**, 648 (1936).

then an atom jumps to another site, becomes detached from the surface—this constitutes the activated state—and finally, escapes into the gas phase. Since the initial state in the reaction is $\frac{1}{2}\text{H}_2$ and the final state is H , the process is endothermic to the extent of one-half the heat of dissociation of molecular hydrogen, *i.e.*, 51.5 kcal. at 0°K . The activation energy of the process under consideration should thus have at least this value; and if E_0 is assumed to be 51.5 kcal., it is possible to calculate the rate of the reaction, at various temperatures, by means of Eq. (98). The surface is assumed to be sparsely covered, so that c_s may be taken as 10^{15} per square centimeter. The results, expressed as atoms $\text{cm}^{-2} \text{sec}^{-1}$, are compared with the experimental rates in Table XLIII, the pressure p being in millimeters

TABLE XLIII.—DISSOCIATION OF HYDROGEN ON A TUNGSTEN SURFACE

Temp., $^\circ\text{K}$.	Rate of dissociation	
	Calc.	Obs.
1148	$3.3 \times 10^{15} \sqrt{p}$	$6.6 \times 10^{15} \sqrt{p}$
1243	1.8×10^{16}	3.0×10^{16}
1378	8.0×10^{16}	1.1×10^{17}
1420	2.4×10^{17}	2.9×10^{17}

of mercury. It is of interest to call attention to the fact that in this particular reaction the simple assumption that the activated state consists of hydrogen atoms permits the absolute rate of dissociation of hydrogen on a tungsten surface to be calculated with an accuracy probably as good as that attained by experiment.

According to the observations of R. C. L. Bosworth⁵⁴ the surface is almost fully covered with hydrogen under the conditions employed in obtaining the data in Table XLIII. Since the formation of atomic hydrogen is not of zero order, it is apparent that, even if the surface as a whole were largely covered, the active centers on which reaction occurs can be only sparsely covered. If the experiments on the extent of coverage of the surface are correct, therefore, the active centers must constitute a fraction only of the total number of tungsten atoms on the

⁵⁴ R. C. L. Bosworth, *ibid.*, **33**, 394 (1937).

surface. In view of the agreement between observed and calculated rates in Table XLIII, the latter being based on the assumption of a bare surface, this fraction must be relatively large.

Comparison of Homogeneous and Heterogeneous Reactions.⁵⁵

The reaction rate per square centimeter of surface for a second-order heterogeneous reaction may be written [cf. Eq. (72)] as

$$v_{\text{het.}} = c_A c_B c_s \frac{kT}{h} \cdot \frac{1}{F_A F_B} e^{-E_{\text{het.}}/RT}, \quad (99)$$

where the reactants are designated by A and B; the partition functions of the activated complex and of the reaction centers have been taken as unity. For the corresponding process occurring entirely in the gas phase, the rate equation, according to the theory of absolute reaction rates, is

$$v_{\text{hom.}} = c_A c_B \frac{kT}{h} \cdot \frac{F_{\ddagger}}{F_A F_B} e^{-E_{\text{hom.}}/RT}. \quad (100)$$

It follows, therefore, that

$$\frac{v_{\text{het.}}}{v_{\text{hom.}}} = \frac{c_s}{F_{\ddagger}} e^{\Delta E/RT}, \quad (101)$$

where ΔE is equal to $E_{\text{hom.}} - E_{\text{het.}}$, *i.e.*, the amount that the activation energy of the homogeneous reaction is greater than that of the heterogeneous process. For 1 sq. cm. of smooth surface, c_s is about 10^{15} whereas the partition function F_{\ddagger} for the activated complex of the homogeneous gas reaction is at least 10^{24} (for hydrogen) and is often of the order of 10^{30} per cubic centimeter; taking 10^{27} as a mean value for F_{\ddagger} , it follows that

$$\frac{v_{\text{het.}}}{v_{\text{hom.}}} \approx 10^{-12} e^{\Delta E/RT}, \quad (102)$$

the heterogeneous rate being that for 1 sq. cm. of surface and the homogeneous rate for 1 cc. of the gaseous reactants. It is obvious, therefore, that, if a heterogeneous reaction is to be as fast as a homogeneous one involving the same reactants at the same pressures, either a very large surface, *viz.*, 10^{12} sq. cm., must be employed or alternatively the activation energy for the

⁵⁵ K. J. Laidler, S. Glasstone and H. Eyring, *J. Chem. Phys.*, **8**, 667 (1940).

heterogeneous reaction must be considerably less than that for the homogeneous process. At a temperature of 500°K., for example, the reaction per square centimeter of surface will have the same rate as the gas reaction per cubic centimeter, only if the activation energy of the former is about 27.6 kcal. less than that of the latter. At lower temperatures the difference would need to be smaller, *e.g.*, 16.5 kcal. at 300°K.

TABLE XLIV.—ACTIVATION ENERGIES FOR HOMOGENEOUS AND HETEROGENEOUS REACTIONS

Decomposition of	Surface	$E_{\text{het.}}$, kcal.	$E_{\text{hom.}}$, kcal.
HI	Au ⁵⁶	25.0	44.0
	Pt ⁵⁷	14.0	
N ₂ O	Au ⁵⁸	29.0	58.5
	Pt ⁵⁹	32.5	
NH ₃	W ⁶⁰	39.0	>80
	Os ⁶¹	47.0	
	Mo ⁶²	32 to 42	
CH ₄	Pt ⁶³	55 to 60	>80

It may appear surprising, at first sight, in view of the much smaller activation energy necessary for a heterogeneous reaction to have the same rate as the corresponding homogeneous one, that catalyzed reactions are frequently so much faster than those which take place entirely in the gas phase. The reason is two-fold: (1) The surface area of the catalyst is very large, so that the reaction is not restricted to 1 sq. cm. as has been assumed in the above calculations. (2) The activation energy for a heterogeneous reaction is generally less than for the same process in the gas phase. This is illustrated by the observed activation energies for a number of reactions, which have been studied both heterogeneously and homogeneously, given in Table XLIV.

⁵⁶ C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 1552 (1925).

⁵⁷ C. N. Hinshelwood and R. E. Burk, *ibid.*, **127**, 2896 (1925).

⁵⁸ Hinshelwood and Prichard, Ref. 38.

⁵⁹ *Idem*, *J. Chem. Soc.*, **127**, 327 (1925).

⁶⁰ C. N. Hinshelwood and R. E. Burk, *ibid.*, **127**, 1116 (1925).

⁶¹ E. A. Arnold and R. E. Burk, *J. Am. Chem. Soc.*, **54**, 23 (1932).

⁶² C. H. Kunsman, *ibid.*, **50**, 2100 (1928).

⁶³ G.-M. Schwab and E. Pietsch, *Z. physik. Chem.*, **121**, 189 (1926).

It is of interest to inquire next into the circumstances that make it possible for the activation energy of the heterogeneous reaction to be less than for that occurring wholly in the gas phase; this may be most easily seen with the aid of a potential-energy diagram. The full line in Fig. 102 represents the variation of potential energy in the decomposition coordinate for the homogeneous reaction, and the dotted curve represents the change during the course of the heterogeneous reaction. The difference between $E_{\text{hom.}}$ and $E_{\text{het.}}$ is seen to be equal to the difference in potential energy between the activated state in

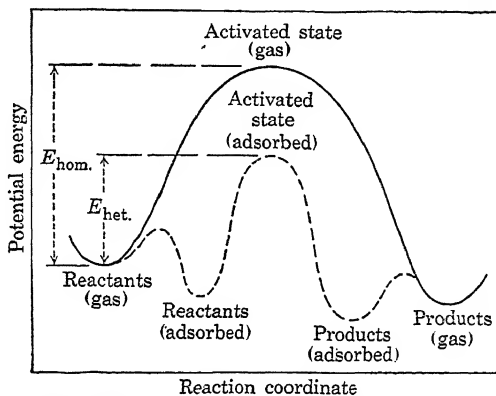


FIG. 102.—Potential-energy curves for the same reaction as a homogeneous and as a heterogeneous process.

the gas phase and on the surface, and hence is equal to the heat of adsorption of the activated complex. If the reactants undergo activated adsorption, it is very probable that the activated complex for the reaction on the surface will consist virtually of atoms or free radicals, and these are likely to have a high energy of adsorption. Under these circumstances, $E_{\text{het.}}$ is liable to be very much lower than $E_{\text{hom.}}$. The decrease in the activation energy for the hydrogen-oxygen reaction and the decompositions of hydrogen iodide and methane on surfaces, as compared with the same homogeneous reactions, has been explained somewhat in this manner.⁶⁴

⁶⁴ M. Polanyi, *Z. Elektrochem.*, **27**, 143 (1921); H. S. Taylor, *J. Phys. Chem.*, **30**, 145 (1926); Schwab and Pietsch, Ref. 63; *Z. physik. Chem.*, **126**, 473 (1927); *Z. Elektrochem.*, **32**, 430 (1926); see also W. G. Frankenburg, *ibid.*, **39**, 269 (1933).

If all the active centers of the surface are covered by one of the products of the reaction or by some other material that is strongly adsorbed and so acts as a poison, the heat of activation is increased by an amount equal to the heat of adsorption of the poison, as seen above. There is some compensation for this increase, however, through the increase of entropy accompanying the desorption of the poison; the situation is very similar to that considered on page 368 in connection with the rate of adsorption on a poisoned surface. As in that instance, the free energy of activation for reaction on such a surface is greater than the value for an unpoisoned surface by an amount equal to the standard free energy of desorption of the poison. It will be noted that in all poisoned reactions a function of the concentration (or pressure) of the poison in the gas phase appears in the denominator of the rate equation, so that the greater the pressure of the retarding gas the slower the reaction rate.

NONUNIFORM SURFACES

Active Centers.—In the preceding discussion the assumption has been made that all the adsorption sites or reaction centers on the surface are the same. The more or less regular decrease in the heat of adsorption with increasing extent of coverage of the surface was attributed to increasing repulsion between the adsorbed molecules (see page 364). It is possible, however, that the variation of the heat of adsorption can be explained in another manner, taking into account the improbability of a uniform surface. It has been pointed out⁶⁵ that a surface must consist of regions of varying degrees of unsaturation; isolated atoms at peaks on the surface and those along edges of crystals will clearly be the most unsaturated, and adsorption will take place preferentially in such positions. Since the most isolated points may be expected to give the highest heats of adsorption, there should be a falling off in this quantity as adsorption proceeds, quite apart from any effect of molecular interaction on the surface.

In addition to the evidence of heats of adsorption, there is ample experimental proof of the nonuniformity of most catalytic

⁶⁵ H. S. Taylor, *Proc. Roy. Soc.*, **108**, A, 105 (1925); *J. Phys. Chem.*, **30**, 145 (1926).

surfaces and of the existence of active centers on which reaction occurs preferentially. Mention may be made in particular of the phenomena associated with the interaction of hydrogen and carbon dioxide on the surface of platinum at about 1000°C. The total adsorption of hydrogen at this temperature is considerable, but that of carbon dioxide is negligible in comparison; at relatively high pressures of carbon dioxide, however, the reaction rate varies as the pressure of the hydrogen and inversely as that of the carbon dioxide.⁶⁶ It is evident that the kinetics of the reaction is determined by the preferential adsorption of the latter, although, as far as the total surface is concerned, the hydrogen gas is adsorbed in larger amounts. It appears, therefore, that the chemical reaction occurs only at certain points, and on these centers carbon dioxide is the more strongly adsorbed of the two reactants. Further, a platinum surface that has been poisoned in this manner by carbon dioxide for the reaction between it and hydrogen remains quite unaffected in its catalytic action on the decomposition of nitrous oxide.

Quantum-mechanical Treatment.⁶⁷—The subject of the non-uniformity of surfaces has also been considered from the theoretical point of view. The potential energy of a system of three to eight sodium atoms, arranged in definite configurations, taken as equal to the energy of the corresponding number of *s*-electrons, has been calculated by the method described in Chaps. II and III, on the assumption that 28.3 per cent of the binding energy is coulombic in nature. The results show that in the gradual building up of a unit body-centered cube of sodium, by the gradual addition of atoms, appreciable activation energies may be involved at certain stages. The growth of the incomplete crystal unit may therefore take place at a measurable rate. Further, the potential energy of the unit cell of sodium was found to be greater than that of the bulk crystalline metal, and hence the abnormal activity of incompletely crystallized portions of a surface can be readily understood. Similar calculations have been made in connection with the growth of the unit cell of copper, and the results indicate that the activation energies would be higher than for sodium. The crystallization of small aggregates should, therefore, require a relatively high tempera-

⁶⁶ Hinshelwood and Prichard, Ref. 46.

⁶⁷ H. S. Taylor, H. Eyring and A. Sherman, *J. Chem. Phys.*, **1**, 68 (1933).

ture; and hence the lack of uniformity of the surface may be expected to persist under normal conditions. Raising the temperature of a metal results in sintering and a reduced activity for adsorption and catalysis; the rate of growth of crystals is increased under these conditions, and the number of unsaturated atoms is consequently diminished.

Variation of Interatomic Distances.⁶⁸—A second factor that gives rise to nonuniformity in the adsorptive properties of a surface, and hence to changes in the heat of adsorption, is the variation of interatomic distances. It was seen on page 343 that the activation energy of adsorption was a function of the distance between adjacent adsorbing centers on the surface, and presumably the heats of adsorption will vary in a similar manner. It is evident that if a surface is not smooth and the space lattice is distorted, as will particularly be the case if impurities are present, a whole range of interatomic distances may be involved. Preferential adsorption will take place in those regions where the optimum separation of centers exists, and the heat of adsorption will decrease as the less favorable regions become covered.

Reaction Rates on Nonuniform Surfaces.—It was seen on page 349 that since the ratio of the partition functions f_{\ddagger}/f_s is approximately unity the only correction necessary in Eq. (8), for the rate of adsorption, or in fact of any surface process, on a nonuniform surface is in the activation energy. The quantity $c_s e^{-\epsilon/kT}$ must be replaced by a sum of terms for each type of site on the surface; thus, Eq. (8) becomes

$$v = c_g \frac{kT}{h} \cdot \frac{1}{F_g} \sum_i c_{s(i)} e^{-\epsilon_i/kT}, \quad (103)$$

where $c_{s(i)}$ is the number of sites of the i th kind per square centimeter of surface and ϵ_i is the activation energy, per molecule, for these sites. The summation may be replaced by integration, thus,

$$v = c_g \frac{kT}{h} \cdot \frac{1}{F_g} \int_{\epsilon_1}^{\epsilon_2} c_s e^{-\epsilon/kT} di, \quad (104)$$

the limits of integration being chosen so that ϵ_{i_1} , written ϵ_1 , is the lowest activation energy, *i.e.*, for the most active reaction sites, and ϵ_{i_2} , written ϵ_2 , is the highest value, *i.e.*, for a flat surface.

⁶⁸ See Ref. 12.

A relationship between the energy of activation and the corresponding number of centers may be derived by adopting a procedure similar to that used by F. H. Constable⁶⁹ and by E. Cremer and G.-M. Schwab.⁷⁰ Suppose that at a particular center the energy of activation for a given reaction is less by an amount dE than at a site on a completely flat surface; according to Constable the extra activity arises from the fact that the atom is displaced to some extent from its equilibrium position. The distribution of active centers will then be related, from this point of view, to the distribution of interatomic distances about a mean value on the nonuniform surface, and the latter can probably be well represented by a Gauss error function. The number of centers $c_s di$, for which the activation energy is between E and $E + dE$ less than at a similar site on a flat surface, is then given by the relationship

$$c_s di = a' e^{-b'E} dE, \quad (105)$$

where a' and b' are constants. If ϵ_2 is, as stated above, the activation energy for a point on the smooth surface and ϵ is the value at *any* active center, then

$$\epsilon_2 - \epsilon = E; \quad (106)$$

and since ϵ_2 is a constant, it follows that Eq. (105) can be written in the form

$$c_s di = a e^{b\epsilon} d\epsilon, \quad (107)$$

a and b being constants. Substituting this value in Eq. (104) and changing the integration limits accordingly, the rate equation becomes

$$v = c_g \frac{kT}{h} \cdot \frac{a}{F_g} \int_{\epsilon_1}^{\epsilon_2} e^{\epsilon(b - \frac{1}{kT})} d\epsilon \quad (108)$$

$$= c_g \frac{kT}{h} \cdot \frac{a}{F_g} \cdot \frac{e^{b(\epsilon_2 - \epsilon_1)}}{b - \frac{1}{kT}} e^{-(\epsilon_2 - \epsilon_1)/kT}, \quad (109)$$

and this can be put into the alternative, approximate form

$$v = c_g B e^{bE'} e^{-E'/RT}. \quad (110)$$

⁶⁹ F. H. Constable, *Proc. Roy. Soc.*, **108**, A, 355 (1925).

⁷⁰ E. Cremer and G.-M. Schwab, *Z. physik. Chem.*, A, **144**, 243 (1929); G.-M. Schwab, *ibid.*, B, **5**, 406 (1929).

The equation for the specific reaction rate is then

$$k = B e^{bE'} e^{-E'/RT}, \quad (111)$$

where B is a constant and E' is the difference in the activation energy, per mole of reactant, for the least active and most active centers. Since Eq. (111) is of the form $k = A e^{-E/RT}$, it is evident that E' may be regarded as the effective, or mean, activation energy for the whole surface; and since the frequency factor A in the rate equation is equivalent to $B e^{bE'}$, it appears that for the nonuniform surfaces the factor A may be expected to be an exponential function of the experimental activation energy. A relationship of this kind has been found in the dehydrogenation of alcohol on copper oxide surfaces and of cyclohexanone, decalin and other substances on various surfaces.⁷¹

It has been seen (page 21) that the frequency factor is related in an exponential manner to the entropy of activation of a reaction; it follows, therefore, that in the cases under consideration there is a simple connection between the activation energy of the process and the entropy of activation. This is another illustration of the fact, also noted in other connections (page 409), that entropy and energy (heat-content) changes are frequently related to one another.

THERMODYNAMIC FORMULATION OF SURFACE PROCESSES⁷²

Entropy of Activation in Adsorption.—According to Eq. (7), the specific rate of adsorption or of a surface reaction in general for a single site on the surface is given by

$$k = \frac{kT}{h} \cdot \frac{f_{\ddagger}}{F_s f_s} \quad (112)$$

$$= \frac{kT}{h} K^{\ddagger}, \quad (113)$$

and by the methods described on page 198 this may be written in the form

$$k = e^{-(\Delta n^{\ddagger}-1)} \frac{kT}{h} e^{-E/RT} e^{\Delta S_c^{\ddagger}/R}, \quad (114)$$

⁷¹ Constable, Ref. 69; E. Cremer, *Z. physik. Chem.*, A, **144**, 231 (1929); A. Balandin, *ibid.*, B, **19**, 451 (1932).

⁷² Kimball, Ref. 13.

where Δn^\ddagger is the increase in the number of molecules accompanying the formation of the activated state, E is the experimental activation energy, equivalent to E_{het} previously discussed, and ΔS_c^\ddagger is the standard entropy of formation of the activated complex, the standard states being unit concentration, *i.e.*, 1 mole per cc. of gas, and 1 mole per sq. cm. of reaction sites and activated complexes. For a reaction involving one molecule of reactant, or for the adsorption of a single gas, Eq. (114) becomes

$$k = e^2 \frac{kT}{h} e^{-E/RT} e^{\Delta S_c^\ddagger/R}. \quad (115)$$

Since the reactant has three degrees of translational freedom, besides rotation, in the gas phase, whereas the activated complex, for either adsorption or reaction, is generally immobile, there will be a considerable loss of entropy accompanying the formation of the activated state. The extent of this loss can be readily estimated in the following manner: for a reaction not involving dissociation,

$$K_c^\ddagger = \frac{f_\ddagger}{F_g f_s} = \frac{1}{\frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{8\pi^2 I kT}{h^2}} e^{-E_0/RT}, \quad (116)$$

it being assumed that the reactant is a diatomic molecule; the partition function of the reaction sites and of the adsorbed activated complexes, together with the vibrational contributions of initial and activated states, are assumed to cancel each other. This will be very close to the truth provided, as appears to be generally the case—for one reason or another—that the activated complex is immobile. Since $\Delta F_c^\ddagger = -RT \ln K_c^\ddagger$, it follows from Eq. (116) that

$$\Delta F_c^\ddagger = -RT \ln \frac{h^3}{(2\pi mkT)^{3/2}} - RT \ln \frac{h^2}{8\pi^2 I kT} + E_0, \quad (117)$$

$$\begin{aligned} \therefore \Delta S_c^\ddagger &\equiv - \left[\frac{\partial(\Delta F_c^\ddagger)}{\partial T} \right]_x \\ &= -R \ln \frac{(2\pi mkTe)^{3/2}}{h^3} - R \ln \frac{8\pi^2 I kTe}{h^2}. \end{aligned} \quad (118)$$

If the adsorbed molecule contains more than three atoms and is nonlinear, so that it has three moments of inertia, A , B and C ,

the rotational term, *i.e.*, the last term on the right-hand side of Eq. (118), becomes

$$R \ln \frac{8\pi^2(8\pi^3 ABC)^{1/2}(kTe)^{3/2}}{h^3}. \quad (119)$$

If the adsorbed molecules were mobile on the surface, the entropy change, due to the loss of one instead of three degrees of translational freedom, would be one-third of that given by the first term on the right-hand side of Eq. (118). Further, if the surface reaction is accompanied by dissociation, which results from the jump of one or both the atoms constituting the adsorbed mole-

TABLE XLV.—TYPICAL VALUES OF ΔS_c^\ddagger ARISING FROM LOSS OF FREEDOM IN ADSORPTION

Type of layer	Degrees of freedom lost	ΔS_c^\ddagger	E.U. per mole
Immobile.....	3 translational	$-R \ln \frac{(2\pi mkTe)^{3/2}}{h^3}$	- 112.8
Immobile (non-linear molecule).	3 rotational	$-R \ln \frac{8\pi^2(8\pi^3 ABC)^{1/2}(kTe)^{3/2}}{h^3}$	- 10.1
Immobile (linear molecule).....	2 rotational	$-R \ln \frac{8\pi^2 I kTe}{h^2}$	- 6.0
Immobile (with dissociation)....	3 translational	$-R \ln \frac{(2\pi mkTe)^{3/2}}{h^{3/2}}$	- 56.4
Mobile.....	1 translational	$-R \ln \frac{(2\pi mkTe)^{1/2}}{h}$	- 37.6

cule from one site to another (page 357), the equilibrium constant between normal and activated states is

$$K_c^\ddagger = \frac{f_\ddagger}{F_g^{1/2} f_s}. \quad (120)$$

The entropy changes are then half the values given by Eqs. (118) and (119); when dissociation occurs simultaneously with adsorption (*cf.* page 357), however, the values are clearly the same as those derived above. The entropies of activation calculated from these equations, the temperature being taken as

300°K., the moments of inertia as 10^{-40} g. cm.² and m as 1 atomic weight unit, are given in Table XLV.

According to the foregoing results the process of adsorption in an immobile layer should result in a decrease of entropy of more than 110 E.U. per mole for a particle of this type; for heavier molecules the entropy change would be still larger. It must be remembered, however, that these values are to a great extent the result of the unusual standard states which are convenient for the present purpose.

By expressing the equation for the rate of adsorption or for a surface reaction in the form of Eq. (115), it is possible to calculate ΔS_c^\ddagger from the experimental rate and the energy of activation, provided that the correct units are employed. This may be compared with the value, analogous to that given in Table XLV, obtained by inserting the correct masses and moments of inertia in Eqs. (118) and (119). Such a treatment, however, would not reveal anything new, for this comparison is precisely the same, except that a different symbolism is used, as that already made previously for rates of adsorption, desorption and chemical reaction. One point of interest may, however, be mentioned. In view of the assumption made that the activated complex for adsorption is an immobile molecule attached to the surface, there should be little difference between activated and final states; the entropy of activation for desorption should thus be numerically small or zero. This expectation is borne out by the limited experimental results that are available.

CHAPTER VIII

REACTIONS IN SOLUTION

THEORY OF ABSOLUTE REACTION RATES

Collision Theory in Solutions.—The early applications of the collision theory to reactions in solution, such as the hydrolysis of acid amides and esters in aqueous solution and the formation of quaternary ammonium salts from *m*- and *p*-nitrobenzyl chlorides and trimethylamine in benzene solution, led to the conclusion that the observed velocities were much less than was to be expected theoretically. If the equation $k = PZ e^{-E/RT}$ is applicable, then, provided that the collision number Z for a bimolecular reaction is the same in solution as in the gas phase, the values of the probability factor P are as low as 10^{-5} to 10^{-10} . At the time these results were obtained, it was commonly believed that P was approximately unity for all bimolecular gas reactions, and hence the small probability factors in solution were attributed to the influence of the solvent. It was found, however, that many processes for which P was small in solution required values of the same order to account for their velocities in the gas phase. It appears, therefore, that there is no fundamental difference between a reaction occurring in solution and that between the same substances in the gaseous state. This should not be taken as implying that the solvent has no influence; its effect is important, as will be evident shortly, but it is improbable that the solute molecules deactivate the activated complexes to any appreciable extent, as was at one time supposed. Deactivation resulting from collisions with the solvent is always just balanced by an equivalent number of activating collisions.

The Rate-determining Step in Solution.—A chemical reaction in solution involves the possibility of at least three slow stages: (1) diffusion of the reacting molecules to one another; (2) reaction between the molecules, with the intermediate formation of an activated complex and (3) diffusion of the products away

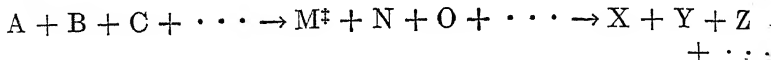
from each other. Diffusion in a liquid may be treated as a rate process requiring a definite activation energy, as will be seen in Chap. IX, but the magnitude of this energy is generally of the order of 5 kcal. The great majority of chemical reactions occurring in solution, however, require an energy of activation of 10 to 20 kcal., and so it is evident that this must be the energy of the second of the three stages enumerated above; step (2) is consequently the rate-determining one for most reactions between dissolved substances. It is probable that processes involving the recombination of ions, which occur very rapidly, require very low activation energies; if such reactions could be studied, it would no doubt be found that diffusion of the ions is often the rate-determining step. There are, in addition, two types of reaction in which diffusion is at least important, if not completely rate-determining; these are certain cases of the quenching of fluorescence in solution (*cf.*, however, page 337) and heterogeneous reactions between a solid and a liquid. Since the rate of diffusion is related to viscosity, the kinetics of processes that are dependent on diffusion will involve the viscosity of the medium. For ordinary chemical reactions, whose rates can be conveniently studied in solution, the viscosity appears to play little part; and so it may be assumed, for the present, that the rate-determining step in solution is the same as for reactions in the gas phase, *viz.*, the formation from the reactants of an activated complex which subsequently decomposes.

Theory of Absolute Reaction Rates.¹—The treatment of chemical reactions in solution by the theory of absolute reaction rates should, in principle, be the same as for gas reactions, with the modification that the partition functions of the reacting species and the activated complex should contain terms which allow for the influence of the environment. There is some uncertainty, however, concerning partition functions of molecules in the liquid phase, and so it has been found more convenient to treat reactions in solution from a less fundamental point of view. It must be pointed out, however, that the difficulty lies solely in an inadequate knowledge of the properties of liquids; for when the theory of the subject has been developed sufficiently

¹ W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **3**, 493 (1935); A. E. Stearn and H. Eyring, *ibid.*, **5**, 113 (1937); K. J. Laidler and H. Eyring, *Ann. New York Acad. Sci.*, **39**, 303 (1940).

and accurate partition functions can be derived, it should be possible to calculate the absolute rates of reactions in solution just as for those occurring in the gas phase.

It has been seen in Chap. IV that the specific rate of the general reaction



where M^\ddagger is the activated complex, N, O, . . . are intermediates, and X, Y, . . . are the final products, is given by the expression

$$k = \kappa \frac{kT}{h} K^\ddagger, \quad (1)$$

where K^\ddagger is the constant for the equilibrium between M^\ddagger , N, O, . . . and A, B, C, . . . In this equation (*cf.* page 190) K^\ddagger is not the true, *i.e.*, the thermodynamic, equilibrium constant, but the corresponding quantity involving concentrations; it follows, therefore, that Eq. (1) should be written

$$k = \kappa \frac{kT}{h} \cdot \frac{c_{M^\ddagger} c_N c_O \dots}{c_A c_B c_C \dots}, \quad (2)$$

where the c terms are the concentrations of the indicated species, the activated complex being treated as a molecule with one degree of vibrational freedom less than normal. The true equilibrium constant K_0^\ddagger is defined by

$$K_0^\ddagger = \frac{a_{M^\ddagger} a_N a_O \dots}{a_A a_B a_C \dots} = \frac{c_{M^\ddagger} c_N c_O \dots}{c_A c_B c_C \dots} \cdot \frac{\alpha_{M^\ddagger} \alpha_N \alpha_O \dots}{\alpha_A \alpha_B \alpha_C \dots}, \quad (3)$$

where the a terms are the activities and the α terms the activity coefficients. By combining Eqs. (2) and (3), it is seen that

$$k = \left(\kappa \frac{kT}{h} K_0^\ddagger \right) \frac{\alpha_A \alpha_B \alpha_C \dots}{\alpha_{M^\ddagger} \alpha_N \alpha_O \dots},^* \quad (4)$$

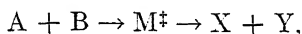
which is the most general form of the specific rate equation. For an ideal gaseous system the activity coefficients are unity, and so Eq. (4) becomes identical with (1); under these conditions

* It is particularly interesting to note that this equation is really a form of Eq. (159), p. 196; K_0^\ddagger is equal to $e^{-\Delta F^\ddagger/RT}$, where $-\Delta F^\ddagger$ is the standard free energy of activation due to internal factors, and the activity coefficient fraction $\alpha_A \alpha_B \alpha_C \dots / \alpha_{M^\ddagger} \alpha_N \alpha_O \dots$ is equivalent to $-\Delta F_{\text{ext}}^\ddagger$ due to external factors, *e.g.*, the medium in which the reaction occurs.

the specific reaction rate, which is equal to $\kappa(kT/h)K_0^\ddagger$, may be represented by k_0 , so that Eq. (4) may be written in the form

$$k = k_0 \frac{\alpha_A \alpha_B \alpha_C}{\alpha_M^\ddagger \alpha_N \alpha_O} \quad (5)$$

This equation is applicable to the given reaction in any one medium, where k_0 is the rate constant at very low pressures, for the gas reaction or, in very dilute solution, for the reaction in the liquid phase, when the substances concerned behave ideally. Since most reactions that are discussed in this chapter are of the type



i.e., in which the two reactants combine to form the activated complex M^\ddagger , with no intermediates, Eq. (5) will be, for present purposes, reduced to the form

$$k = k_0 \frac{\alpha_A \alpha_B}{\alpha_\ddagger}, \quad (6)$$

where α_\ddagger represents the activity coefficient of the activated complex.

Activity Coefficients.—If it is required to compare the velocity of a reaction in one medium with that in another, care must be taken in defining the activity coefficients. The most convenient procedure is to compare the rates in one solvent or in a series of solvents with that in the gas phase; hence, the activity coefficients in solution must be defined with respect to the ideal gas at 1 atm. pressure as the standard state. The appropriate activity coefficient α is then defined by

$$\alpha = \frac{\text{conc. of solute in the vapor above the solution}}{\text{conc. of solute in the solution}}, \quad (7)$$

the pressure of the solute above the solution being so low that the vapor may be regarded as behaving ideally. It is to be understood, of course, that according to Raoult's law the concentrations should be expressed in mole fractions. In the study of solutions, it is often the practice to take the pure liquid as the standard state; the corresponding activity coefficient γ is then defined as follows:

$$\gamma = \frac{\text{conc. of solute in the solution if it were ideal}}{\text{conc. of solute in the actual solution}}. \quad (8)$$

If the relationship between α and γ is represented by the expression $\alpha = \beta\gamma$, then Eq. (6) becomes

$$k = k_0 \frac{\beta_A \beta_B}{\beta_{\ddagger}} \cdot \frac{\gamma_A \gamma_B}{\gamma_{\ddagger}}. \quad (9)$$

Since β is equal to α/γ , it is clear from Eqs. (7) and (8) that it must be a constant for every substance at any given temperature; it follows, therefore, that Eq. (9) can be written in the form

$$k = k'_0 \frac{\gamma_A \gamma_B}{\gamma_{\ddagger}}. \quad (10)$$

Since k'_0 is dependent only on the reactants A and B and the activated complex, it is evidently a constant for the given reaction, at a definite temperature, irrespective of the nature of the medium in which k is measured. For two different solvents, designated by suffixes I and II, it follows that

$$\frac{k_I}{k_{II}} = \frac{(\gamma_A \gamma_B / \gamma_{\ddagger})_I}{(\gamma_A \gamma_B / \gamma_{\ddagger})_{II}}, \quad (11)$$

where the activity coefficients are in each case referred to pure A, B and the activated complex as the standard states. It is possible to write Eq. (11) in a different form by making use of the fact derived from Eq. (8) that the ratio of the γ 's in two solvents is equal to the ratio of the concentrations of the solute in the vapors above the two solutions; this is also equal to the ratio of the partial pressures of the solutes in the solutions, and so

$$\frac{k_I}{k_{II}} = \frac{\pi_A \pi_B}{\pi_{\ddagger}}, \quad (12)$$

where π for each species is the ratio of the partial pressures in solvents I and II at the concentrations involved in the reaction.

The Brønsted-Bjerrum Equation.—For the comparison of rates of a particular reaction in a given solvent under such conditions that the activities are altered by the addition of salts, it is convenient to define the activity coefficient f with respect to the infinitely dilute solution as the standard state. By adopting the method given above, *i.e.*, by expressing α in terms of f and the activity coefficient of the dilute solution with reference to the ideal gas, it follows that

$$k = k_0^* \frac{f_A f_B}{f_{\ddagger}}, \quad (13)$$

where k_0^* is the rate constant in the given solvent at infinite dilution when the activity coefficients are all unity. The same result may be obtained from Eq. (6), since this applies to any one medium; if k_0 refers to the highly dilute solution, then α is identical with f , and so Eq. (13) is identical with the well-known relationship first derived in different ways by J. N. Brønsted² and by N. Bjerrum.³

Influence of Environment.—As implied by the foregoing discussion, there are several aspects of the influence of the environment on the rate of a reaction. (1) The magnitude of the velocity in solution may be compared with that in the gas phase. (2) The rates in different solvents may be considered. (3) The reaction may be examined in one particular solvent, *e.g.*, water, and the activities of the reactants and of the activated complex changed by altering the ionic strength or dielectric constant of the medium. The equations already derived show that the problem reduces to an evaluation of the activity coefficients under different conditions; these can be determined experimentally as far as the reactants are concerned, but there are no means whereby the activity coefficient of an activated complex can be obtained by direct measurement. Provided that the solution is dilute, the activity coefficient of an ion can be related to the charge by means of the Debye-Hückel equations; if these apply to the complex, then, since its charge is known to be equal to the algebraic sum of the charges carried by the reactants, its activity coefficient can be calculated. The activity coefficient can also be changed by altering the dielectric constant of the medium, *e.g.*, by the addition of ethyl alcohol; and the value can again be derived from the appropriate equations based on the Debye-Hückel theory. It is in connection with the studies of ionic reactions, therefore, that a comparison can be made between the observed and calculated effects of environment on reaction velocity. For processes involving neutral molecules only or ions and neutral molecules, a quantitative treatment can be carried through if the molecules are highly polar; but in other instances qualitative discussion only is possible. Reactions in solution are, therefore, most advantageously considered with reference to the type of reactant concerned. Before doing so,

² J. N. Brønsted, *Z. physik. Chem.*, **102**, 109 (1922); **115**, 337 (1925).

³ N. Bjerrum, *ibid.*, **108**, 82 (1924).

however, certain general aspects of the problem of solubility influence on reaction rates will be examined.

Reaction Rates and Solubility.—According to the work of O. Dimroth⁴ on the intramolecular transformation of the aci-form of 1-phenyl-5-oxytriazole carboxylic ester into its neutral form in a number of solvents, the specific rate constant is related to the solubility s_A of the reactant by an equation of the form

$$k = \text{const.} \frac{1}{s_A}, \quad (14)$$

which is in agreement with the rule originally proposed by J. H. van't Hoff (1898). The activity coefficient γ of a solute, with reference to the pure liquid as the standard state, is equal to the reciprocal of the saturation solubility, expressed in mole fractions, in the given solvent. Substituting $1/s$ for the γ terms in Eq. (10), it follows that

$$k = k_0' \frac{s_{\ddagger}}{s_A s_B}. \quad (15)$$

This equation would become identical with Eq. (14), for a single reactant, if s_{\ddagger} were constant; the solubility of the activated complex is presumably, in this instance, almost independent of the solvent employed. This result is probably fortuitous, however, for it has been established that Eq. (14) and similar equations are of very limited applicability.⁵

Comparison of Reaction Rates in Gas Phase and in Solution.—It will be seen from Eq. (6) that the ratio of the specific rate of a given reaction in solution to that of the same process taking place in the gas phase is given by

$$\frac{k_s}{k_g} = \frac{\alpha_A \alpha_B}{\alpha_{\ddagger}}, \quad (16)$$

where k_s , the rate constant in solution, is written for k and k_g the specific rate in the gas phase is substituted for k_0 . If the two rates are to be equal, the activity coefficient factor

⁴ O. Dimroth, *Ann.*, **377**, 127 (1910).

⁵ H. Eyring and F. Daniels, *J. Am. Chem. Soc.*, **52**, 1472 (1930); see also E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, 1933.

must be unity. It is easy to see how this might arise for a unimolecular reaction, for which Eq. (16) becomes

$$\frac{k_g}{k_o} = \frac{\alpha_A}{\alpha_{\ddagger}} \quad (17)$$

If the reactant and the activated complex have similar structures, then α_A and α_{\ddagger} will not differ greatly and the rate of reaction in solution will be almost the same as that in the gas phase. This is apparently true for the decomposition of nitrogen pentoxide in a number of solvents,⁶ as is shown by the results recorded in Table XLVI. The energies of activation E are also almost constant.

TABLE XLVI.—DECOMPOSITION OF NITROGEN PENTOXIDE IN GAS PHASE AND IN SOLUTION AT 20°C.

Solvent	$k \times 10^5$	E , kcal.
(Gas phase).....	1.65	24.7
Nitromethane.....	1.53	24.5
Bromine.....	2.15	24.0
Pentachlorethane.....	2.20	25.0
Carbon tetrachloride....	2.35	24.1
Ethylene chloride.....	2.38	24.4
Chloroform.....	2.74	24.6
Ethylidene chloride.....	3.22	24.9
Nitrogen tetroxide.....	3.44	25.0

In propylene dichloride and nitric acid solutions the decomposition of nitrogen pentoxide is unusually slow,⁷ the rate constants being 7.35×10^{-5} and 1.97×10^{-5} respectively at 45°,^{*} and the energies of activation are high, *viz.*, 28.0 and 28.3 kcal. These results may be due to the formation of complexes between the reactant and solvent; as will be seen shortly (page 415), such compound formation may increase the energy of activation of the reaction.

The isomeric change of *d*-pinene to dipentene is a unimolecular process that has been studied in solution as well as in the gas phase.⁸ The rate constant at 218°C. is 5.1×10^{-4} for the gaseous

⁶ Eyring and Daniels, Ref. 5.

⁷ H. Eyring and F. Daniels, *J. Am. Chem. Soc.*, **52**, 1486 (1930).

^{*} The specific rate in the gas phase at 45° is 4.73×10^{-4} .

⁸ D. F. Smith, *ibid.*, **49**, 43 (1927).

reaction; and values of 7.8×10^{-4} , 8.0×10^{-5} and 8.7×10^{-5} have been obtained in petrolatum, acetophenone and α -methyl-naphthalene solutions, respectively. In this reaction the reactant and product are both hydrocarbons and their solubilities, as well as those of the activated complex, will be similar in different solvents; it is, therefore, reasonable to suppose that α_A/α_+ , and hence the ratio of the rates in the gas phase and in solution, will be of the order of unity.

The solubility s_g of a substance in the gaseous phase in a liquid solvent may be represented by an equation of the form

$$s_g = B e^{-\Delta H_s/RT} \quad (18)$$

where B is equal to $e^{\Delta S/R}$, ΔS being the standard entropy,* and ΔH_s is the heat of solution of the given solute in the particular solvent. The quantity s_g is almost the same as the reciprocal of the activity coefficient with respect to the ideal gas as standard state; and so if the corresponding value of $1/s_g$ as given by Eq. (18) is substituted for the α terms in Eq. (16), it follows that

$$\frac{k_s}{k_g} = \frac{s_+}{s_A s_B} = \frac{B_+}{B_A B_B} e^{-\Sigma \Delta H_s/RT}, \quad (19)$$

where $\Sigma \Delta H_s$ is equal to $\Delta H_+ - \Delta H_A - \Delta H_B$.

If the reaction rates in solution and in the gas phase are written in the familiar form $k = A e^{-E/RT}$, then

$$\frac{k_s}{k_g} = \frac{A_s}{A_g} e^{-(E_s - E_g)/RT}, \quad (20)$$

where E_s and E_g are the activation energies for the reaction in solution and in the gas phase, respectively. Comparison of Eqs. (19) and (20) indicates that the difference in the activation energies is equivalent to $\Sigma \Delta H_s$, which represents the difference in the heats of solution of initial and activated states. If $\Delta H_A + \Delta H_B$ is equal to ΔH_+ , so that $\Sigma \Delta H_s$ is zero, the energy of activation for the given reaction should be the same in solution as in the gas phase, and

$$\frac{k_s}{k_g} = \frac{B_+}{B_A B_B}. \quad (21)$$

* The increase of entropy ΔS refers to equal volume concentrations in gas and solution.

It appears, from experimental data on the solubilities⁹ of various gases, that the entropy factor B is approximately 10^{-2} for a number of substances; if this figure is substituted for B_A , B_B and B_{\ddagger} , it is seen that¹⁰

$$\frac{k_s}{k_a} \approx 10^2. \quad (22)$$

A bimolecular reaction should thus be somewhat faster in solution than in the gas phase, provided that $\Sigma \Delta H_s$ is negligibly small and the activation energy is the same under both conditions. The facts seem to indicate that any effect of this kind is small.

The information obtained from gas solubilities may be applied in a somewhat different way. It has been established empirically that heats and entropies of solution are related in a linear manner by the equation

$$T \Delta S = \rho \Delta H_s + \sigma, \quad (23)$$

where ρ and σ are constants. Since the factor B in Eq. (18) is equivalent to $e^{\Delta S/R}$, it follows from Eqs. (21) and (23) that

$$\frac{k_s}{k_a} = e^{\Sigma \Delta S/R} = e^{\Sigma \sigma/RT}, \quad (24)$$

provided that $\Sigma \Delta H_s$ is zero, as assumed above; the quantity $\Sigma \sigma$ is equal to $\sigma_{\ddagger} - \sigma_A - \sigma_B$. For many gases the value of σ lies within the range -470 to -840 cal. at $25^\circ\text{C}.$; and by taking an approximate mean value of -650 , it is seen that¹¹

$$\frac{k_s}{k_a} \approx e^{650/RT} \quad (25)$$

At ordinary temperatures, the rate of a given bimolecular reaction in solution may thus be expected to be two or three times as fast as in the gas phase. It should be emphasized that this conclusion can hold only for the condition that $\Sigma \Delta H_s$ is small or zero and the energy of activation is the same for the gas reaction as for that in solution. If the activated state differs greatly in polar nature or internal pressure from the reactants, so that the B values in Eq. (21) or the σ values in Eq. (24) are

⁹ J. Horiuti, *Z. Elektrochem.*, **39**, 22 (1933).

¹⁰ M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).

¹¹ *Idem, ibid.*, **32**, 1333 (1936); R. P. Bell, *ibid.*, **33**, 496 (1937); **35**, 324 (1939); *Ann. Rep. Chem. Soc.*, **36**, 82 (1939).

not similar, then the foregoing conditions will not apply. Further, if either the reactants or the activated complex are appreciably solvated in solution, the energy of activation will probably be different from that in the gas phase (*cf.* page 416).

It may be concluded however that, in general, apart from processes of an unusual character, the rate of a bimolecular reaction should be of the same order in solution as in the gas phase. This is apparently true for the decomposition of chlorine monoxide, although it is not strictly a simple bimolecular reaction, the decomposition of ozone uncatalyzed and catalyzed by chlorine, and the decomposition of ethylene iodide, all in carbon tetrachloride solution. Certain Diels-Alder reactions have approximately the same rates in benzene, carbon tetrachloride and carbon disulfide as in the gas phase, and this is also true for the conversion of *para*- to *ortho*-hydrogen catalyzed by oxygen and by nitric oxide in aqueous solution.¹²

REACTIONS BETWEEN NEUTRAL MOLECULES

Regular Solutions.—For an ideal solution, which is defined as one obeying Raoult's law, the relationship

$$F_i - F^\circ = RT \ln N \quad (26)$$

holds for each component, where F_i is its partial molal free energy in the ideal solution, F° is the value in the standard state, *i.e.*, pure liquid, and N is the mole fraction. For a real solution,

$$\bar{F} - F^\circ = RT \ln a, \quad (27)$$

where a is the activity; hence,

$$\bar{F} - \bar{F}_i = RT \ln \frac{a}{N} = RT \ln \gamma. \quad (28)$$

The evaluation of the activity coefficient γ thus requires a knowledge of the partial molal free energies in the actual solution and in the ideal solution at the same concentration of the component under consideration. Since, by thermodynamics,

$$\Delta F = \Delta H - T \Delta S,$$

¹² For review and references, see R. P. Bell, *Ann. Rep. Chem. Soc.*, **36**, 82 (1939).

it follows from (28) that

$$(\bar{H} - \bar{H}_i) - T(S - S_i) = RT \ln \gamma, \quad (29)$$

so that the problem can be divided into two parts, *viz.*, the evaluation of (1) the heat and (2) the entropy of transfer from the actual solution to the ideal solution at the same concentration.

The concept of "regular solutions," introduced by J. H. Hildebrand¹³, has permitted a simplification of the subject in certain cases. A regular solution is defined as one in which the distribution and orientation of the molecules of solute and solvent are completely random, there being no association or combination. For such a solution the entropy of mixing the constituents is given by $R(N_1 \ln N_1 + N_2 \ln N_2)$, which is the same as for an ideal solution, and so $\bar{S} - \bar{S}_i$ is zero; Eq. (29) then reduces to

$$\bar{H} - \bar{H}_i = RT \ln \gamma, \quad (30)$$

for a regular solution. For a liquid system, $\bar{H} - \bar{H}_i$ may be replaced by $\bar{E} - \bar{E}_i$ where the \bar{E} terms are the internal energies, since the change in volume on transferring one mole of solute from the ideal to the real solution is probably negligible. Further, the difference in internal energy may be replaced by the difference in potential energy, so that it is possible to write Eq. (30) as

$$\Delta E = RT \ln \gamma, \quad (31)$$

where ΔE is the difference in potential energy between one mole of component in the actual solution and in the ideal solution.

Attractive Forces.—The difference in potential energy depends on differences in the molecular volumes of the components and on the attractive forces between the molecules. These forces may be divided into two groups: there are those, on the one hand, of short range, generally called the van der Waals or London (dispersion) forces, which exist for all molecular species; and, on the other hand, there are the long-range forces, due to electrostatic attraction, which are of appreciable magnitude only for molecules having relatively high dipole moments. Disregarding, for the present, the electrostatic forces, since these are supposed to be absent from regular solutions, the attraction

¹³ J. H. Hildebrand, *J. Am. Chem. Soc.*, **51**, 66 (1929).

between molecules may be regarded as being entirely of the van der Waals type, the attraction potential being given by k/r^6 , where k is a constant and r is the distance between the two molecules.¹⁴ On this basis, neglecting the repulsive potential, which operates at very small intermolecular distances, and assuming that the molecules possess spherical symmetry, G. A. Scatchard¹⁵ and J. H. Hildebrand and S. E. Wood¹⁶ derived relationships that may be written in the form

$$RT \ln \gamma_1 = v_1 \left(\frac{N_2 v_2}{N_1 v_1 + N_2 v_2} \right)^2 \left[- \frac{2E_{12}}{(v_1 v_2)^{1/2}} + \frac{E_{11}}{v_1} + \frac{E_{22}}{v_2} \right], \quad (32)$$

where v is the molar volume and N the mole fraction of the species designated by the subscripts 1 and 2. The E terms are potential energies related to the attractive forces between the molecules; E_{11} and E_{22} refer to attraction between molecules of the same kind, and E_{12} refers to that between molecules of different kinds.

If the approximation is made of taking the attraction between two different molecules as the geometric mean of the attractions between similar molecules, then

$$E_{12} = (E_{11} E_{22})^{1/2}, \quad (33)$$

and Eq. (32) becomes

$$RT \ln \gamma_1 = v_1 \left(\frac{N_2 v_2}{N_1 v_1 + N_2 v_2} \right)^2 \left[\left(\frac{E_{11}}{v_1} \right)^{1/2} - \left(\frac{E_{22}}{v_2} \right)^{1/2} \right]^2. \quad (34)$$

The potential-energy terms E_{11} and E_{22} may be replaced by the energy of vaporization of the liquid, so that it should be possible to evaluate the activity coefficient of each component of a mixture from a knowledge of its molar volume and heat of vaporization. It must be emphasized that Eq. (34) applies only to a regular solution, *i.e.*, to one in which the molecular distribution is random; various attempts have been made to allow for the possible "ordering," *i.e.*, lack of randomness, in solutions that are not regular.¹⁷ The entropy terms that result

¹⁴ F. London, *Z. physik. Chem.*, **B**, **11**, 221 (1930).

¹⁵ G. Scatchard, *Chem. Rev.*, **8**, 321 (1931).

¹⁶ J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933).

¹⁷ E. A. Guggenheim, *Proc. Roy. Soc.*, **148**, **A**, 304 (1935); G. S. Rushbrooke, *ibid.*, **166**, **A**, 294 (1938); J. G. Kirkwood, *J. Phys. Chem.*, **43**, 94 (1939).

from ordering appear to be quite small and so may be neglected in most cases¹⁸; hence, Eq. (34) may be employed, as a first approximation, for solutions of all types.*

In order to apply the activity coefficient derived from Eq. (34) to the study of reaction rates, it would be necessary to have information concerning the properties of the activated complex that is not available. Although the activated complex must have properties intermediate between those of reactants and resultants, there is little doubt (see page 419) that it frequently resembles one much more than the other; if a simplifying assumption of this type is made, it is possible to arrive at some interesting general conclusions.

Reaction Rate and Internal Pressure.—The quantities E/v in Eq. (34) are approximately equal to a/v^2 , where a is the van der Waals attraction constant, and hence to the internal pressure, or cohesion, of the liquid. If the solution under consideration is not too concentrated, the term N_1v_1 for the solute may be neglected in comparison with N_2v_2 for the solvent, and so Eq. (34) can be written

$$RT \ln \gamma_1 = v_1(P_1^{1/2} - P_2^{1/2})^2 = v_1\Delta, \quad (35)$$

where P_1 and P_2 are the internal pressures of the two constituents of the solution; Δ is an abbreviation for the expression $(P_1^{1/2} - P_2^{1/2})^2$, and since it is always positive it depends only on the numerical difference in the internal pressures of solute and solvent. Upon taking logarithms of Eq. (10), it is seen that

$$\ln k = \text{const.} + \ln \gamma_A + \ln \gamma_B - \ln \gamma_{\ddagger}; \quad (36)$$

if the values of $\ln \gamma$ given by equation (35) are inserted, it follows that

$$RT \ln k = \text{const.} + v_A\Delta_A + v_B\Delta_B - v_{\ddagger}\Delta_{\ddagger} \quad (37)$$

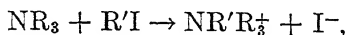
at constant temperature. The influence of a solvent on the reaction velocity is, as seen above, dependent on its effect on the activity coefficients, and according to Eq. (37) this is determined by the molal volumes and the Δ (internal pressure)

¹⁸ Cf. Kirkwood, Ref. 17.

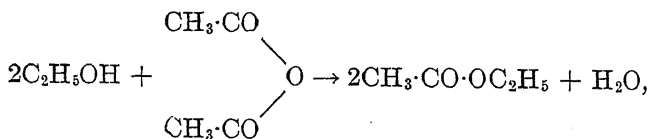
* It has been estimated that when the departure from random distribution is so large that the liquid system is on the point of separating into two phases, the error of Eq. (34) is only about 15 per cent.

terms. Since the molal volumes generally do not vary greatly, it is seen that the specific rate constant is determined, to a great extent, by the difference between the internal pressure of the solvent and the internal pressures of the reactants and activated complex. If the internal pressure of the solvent is close to the values for the reactants, *i.e.*, if Δ_A and Δ_B are small, but appreciably different from that of the activated complex, the factor $v_A\Delta_A + v_B\Delta_B - v_{\ddagger}\Delta_{\ddagger}$ will have a relatively large negative value; hence, according to Eq. (37), the reaction rate in this solvent will be small. If, on the other hand, the solvent has an internal pressure the same as that of the activated complex but different from the internal pressures of the reactants, then the expression $v_A\Delta_A + v_B\Delta_B - v_{\ddagger}\Delta_{\ddagger}$ will have a large positive value, and the reaction rate will be high. By making the assumption that the activated complex resembles the products of the reaction the following rule concerning solvent influence, first enunciated empirically by M. Richardson and F. G. Soper,¹⁹ can be readily understood²⁰: if the reaction is one in which the products are substances of higher internal pressure than the reactants, then it is accelerated by solvents of high internal pressure.

In reactions of the Menschutkin type, involving the formation of a quaternary ammonium salt from a tertiary amine and an alkyl halide, *e.g.*,



the internal pressure of the activated state is likely to be greater than the internal pressures of the reactants,* whereas in the esterification of ethyl alcohol by acetic anhydride,



it is probable that the reverse is the case. The effects of solvents on these two reactions might thus be expected to run in opposite

¹⁹ M. Richardson and F. G. Soper, *J. Chem. Soc.*, 1873 (1929).

²⁰ S. Glasstone. *ibid.*, 723 (1936).

* In general, for reactions of the type $\text{A} + \text{B} \rightarrow \text{C}$, the activated complex may be expected to resemble C rather than $\text{A} + \text{B}$.

directions. This is confirmed, in a general manner, by the results in Table XLVII.²¹

TABLE XLVII.—INFLUENCE OF SOLVENTS ON SPECIFIC REACTION RATES

Solvent	Triethylamine and ethyl iodide (100°C.)	Acetic anhydride and ethyl alcohol (50°C.)
Hexane.....	0.00018	0.0119
Carbon tetrachloride.....	0.0113
Chlorobenzene.....	0.023	0.0053
Benzene.....	0.0058	0.0046
Chloroform.....	0.0040
Anisole.....	0.040	0.0029
Nitrobenzene.....	70.1	0.0024

It is clear that, as a rough approximation, the higher the internal pressure of the solvent the slower is the esterification but the more rapid is the formation of the quaternary ammonium salt, as is to be expected from the discussion above. There are, however, marked deviations which are no doubt due to the fact that in the derivation of Eq. (34), from which Eq. (37) was obtained, electrostatic forces were neglected; this is certainly not justifiable, as will be seen later. Nevertheless, the rule concerning internal pressure and the influence of solvent on reaction velocity is in qualitative agreement with experiment in many instances; among these, mention may be made of the dissociation of sulfonium salts into sulfide and halide²² and of the reaction of the trichloroacetate ion with the solvent, *e.g.*, water, ethyl alcohol or aniline, to yield chloroform.²³ In both these reactions the activated state has probably a lower internal pressure than the reactants, and solvents of high internal pressure tend to slow down the reaction rates.

Solvation Effects.—An important matter to consider in connection with the influence of solvent on reaction velocity is the possibility of solvation of the substances concerned in the

²¹ Data from N. Menshutkin, *Z. physik. Chem.*, **6**, 41 (1890); F. G. Soper and E. Williams, *J. Chem. Soc.*, 2297 (1931).

²² E. D. Hughes and C. K. Ingold, *ibid.*, 244 (1935).

²³ F. H. Verhoek, *J. Am. Chem. Soc.*, **56**, 571 (1935).

reaction.* Suppose curve I in Fig. 103 represents the potential-energy curve for a given reaction in a particular solvent in which none of the reactants or the activated complex is solvated.

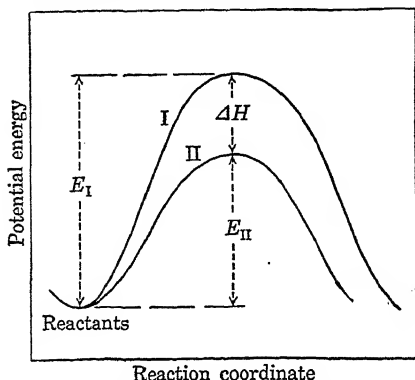


FIG. 103.—Potential-energy curves for a reaction in which the activated complex is not solvated (I) and solvated (II).

If in another solvent the activated complex is solvated but the reactants are unaffected, the potential-energy curve will now be as shown at II; provided that no other factors enter which

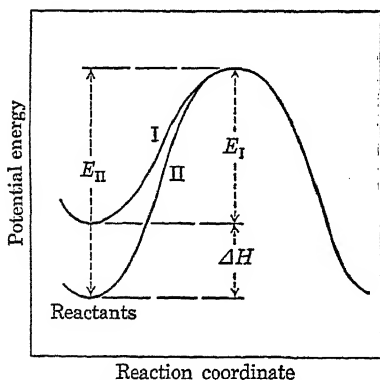


FIG. 104.—Potential-energy curves for a reaction in which the reactants are not solvated (I) and solvated (II).

have an appreciable influence on the activation energy of the reaction, the maximum of the curve will be lowered by an amount ΔH equal to the heat of solvation of the activated complex. The energy of activation when the complex is solvated (E_{II}) is thus lower than that (E_I) for the reaction in a solvent in which there is no solvation. Apart from the influence of other factors, therefore, solvation of the activated complex will tend

to bring about an increase in the reaction rate.

If the reactants that are unsolvated in I are solvated in II but the activated complex is solvated in neither, then the potential-energy curves will have the form indicated in Fig. 104.

* Systems of this type cannot, of course, constitute "regular solutions."

It is evident that solvation of one or more of the reactants will result in an increase of the activation energy, and the reaction will be retarded. It can be readily seen, further, that if both the reactants and the activated complex are solvated, there may be little change in the activation energy, and the influence on reaction velocity will be small. Attention may be called, finally, to the fact that the solvation of the products has no direct influence on the rate of reaction.

The effect of solvation of the activated complex may account for the abnormally high rate of the Menschutkin reaction in nitrobenzene, as recorded in Table XLVII. As already seen, in the combination of an alkyl halide with a tertiary amine the activated complex undoubtedly resembles the product; it is, therefore, probably solvated to a considerable extent in such solvents as nitrobenzene, whereas the reactants are unsolvated. Apart from changes brought about in the activity coefficients, it is to be expected, therefore, that the rate of the reaction under consideration will be high in nitrobenzene.

Entropy of Activation.—The existence of the solvation factor is brought to light in an interesting manner in the study of the reaction between triethylamine and ethyl bromide in acetone-benzene mixtures.²⁴ It was seen on page 199 that according to the theory of absolute reaction rates the specific rate of a reaction in solution may be written

$$k = e \frac{kT}{h} e^{-E_{\text{exp.}}/RT} e^{\Delta S^\ddagger/R}, \quad (38)$$

consequently, the frequency factor A in the equation

$$k = A e^{-E_{\text{exp.}}/RT}$$

may be expressed by

$$A \equiv e \frac{kT}{h} e^{\Delta S^\ddagger/R}, \quad (39)$$

and so, provided that the specific reaction rate and the experimental energy of activation are known, it is possible to calculate ΔS^\ddagger , the entropy of activation. The results obtained in this manner for the triethylamine-ethyl bromide reaction are recorded in Table XLVIII.²⁵

²⁴ A. von Hemptinne and A. Bekaert, *Z. physik. Chem.*, **28**, 225 (1895).

²⁵ Wynne-Jones and Eyring, Ref. 1.

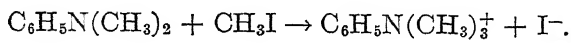
It is seen that the entropy of activation remains almost constant over the range from 20 to 100 per cent of acetone in the solvent*; as long as there are sufficient acetone molecules to surround the activated complex, the entropy of activation should not change appreciably, and this is presumably true provided that the solvent contains at least one-fifth of acetone. In view of the polar nature of the complex, it will probably be solvated to a negligible extent in benzene, and the change in the solvation is accompanied by a marked decrease in activation entropy in this solvent as compared with those containing

TABLE XLVIII.—ENTROPIES OF ACTIVATION IN ACETONE-BENZENE MIXTURES

Acetone, per cent	$E_{\text{exp.}}$, kcal.	ΔS^\ddagger , E.U.
100	11.7	-43.3
80	12.1	-42.3
50	12.0	-43.6
20	12.2	-44.4
0	11.2	-50.1

appreciable proportions of acetone. It will be recalled that a large negative entropy of activation means a slow reaction (page 22), and hence the change in passing from the acetone solutions to pure benzene is in harmony with the general principles already deduced. It is true that the activation energy decreases to some extent at the same time, but this is insufficient to compensate for the change in the entropy of activation.

Although the entropy change of the complete reaction in this case, *i.e.*, triethylamine and ethyl bromide, is not known for the purpose of comparison with the entropy of activation, the data are available²⁶ for the analogous reaction



From the known reaction velocity in nitrobenzene at 60°C. the entropy of activation is -36.1 whereas the difference in entropy between products and reactants is -37.1 E.U. This indicates

* An error of 1 kcal. in $E_{\text{exp.}}$ would correspond to an error of about 3 E.U. in ΔS^\ddagger .

²⁶ H. Essex and O. Gelorimini, *J. Am. Chem. Soc.*, **48**, 882 (1926).

clearly that the activated complex in this reaction must be very similar in structure to the quaternary ammonium salt obtained as product, in agreement with the assumption already made.

DIPOLE MOLECULES

Influence of Dielectric Constant.—The attraction between two dipolar molecules, due to the so-called "orientation effect," is proportional to μ^4 , where μ is the dipole moment; hence, it is evident that the effect of electrostatic forces will become much more marked as the dipole moment increases. By neglecting the short-range van der Waals forces and attributing the deviations from ideal behavior solely to electrostatic forces, J. G. Kirkwood²⁷ was able to calculate the free energy of transfer of a strong dipole from a medium of dielectric constant unity to one of dielectric constant D . This quantity is related to the activity coefficient α for which the dilute gas, *i.e.*, a medium of dielectric constant unity, is the standard state; for a symmetrical charge distribution within the molecule the result is, for a single molecule,

$$\Delta F = kT \ln \alpha = -\frac{\mu^2}{r^3} \cdot \frac{D-1}{2D+1}, \quad (40)$$

where r is the molecular radius. The general accuracy of this equation has been confirmed by the determination of activity coefficients from the vapor pressures of solutions of polar substances in nonpolar solvents; the plot of $\ln \alpha$ against $(D-1)/(2D+1)$ usually approximates to a straight line, although deviations are sometimes observed in media of low dielectric constant.²⁸ If to the expression in Eq. (40) is added a quantity Φ for the deviation from ideal behavior due to nonelectrostatic forces, the result is

$$kT \ln \alpha = -\frac{\mu^2}{r^3} \cdot \frac{D-1}{2D+1} + \Phi. \quad (41)$$

The corresponding activity coefficients may be substituted in Eq. (6), when it is seen that, for the reaction $A + B \rightarrow M^\ddagger \rightarrow$ products,

$$\ln k = \ln k_0 - \frac{1}{kT} \cdot \frac{D-1}{2D+1} \left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} \right) + \frac{\sum \Phi}{kT}, \quad (42)$$

²⁷ J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

²⁸ For summary, see A. R. Martin, *Trans. Faraday Soc.*, **33**, 191 (1937).

where $\Sigma \Phi$ is written for $\Phi_A + \Phi_B - \Phi_{\ddagger}$.²⁹ If the nonelectrostatic forces are small in comparison with the others, $\Sigma \Phi$ may be neglected as a first approximation; it is then apparent that the plot of $\log k$ against $(D - 1)/(2D + 1)$ should be a straight line for the same reaction carried out in different media. The dielectric constant D is actually that of the solution, but if this is dilute it may be replaced by that of the pure solvent; this has been done in the cases considered below.

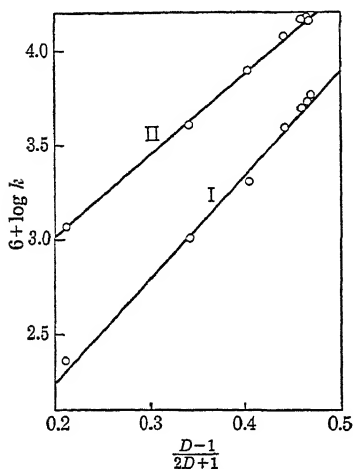


FIG. 105.—Dependence of specific reaction rates on dielectric constant in benzene-alcohol mixtures.

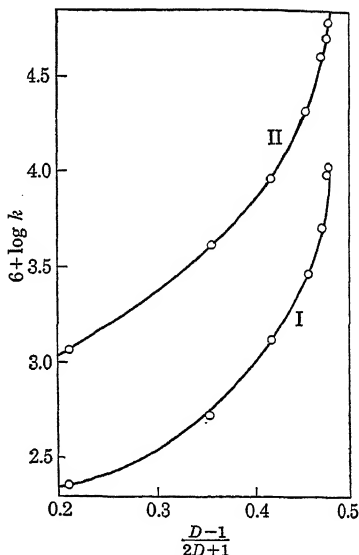


FIG. 106.—Dependence of specific reaction rates on dielectric constant in benzene-nitrobenzene mixtures.

The accuracy of Eq. (42) may be tested in another manner by writing $K_0^\ddagger(kT/h)$ for k_0 , as seen in Eq. (5), the transmission coefficient being taken as unity; thus, the Φ terms being neglected, Eq. (42) becomes

$$\ln k = \ln K_0^\ddagger + \ln \frac{kT}{h} - \frac{1}{kT} \cdot \frac{D - 1}{2D + 1} \sum \frac{\mu^2}{r^3}, \quad (43)$$

so that the plot of $\log k$ against $(D - 1)/(2D + 1)$ should be linear. The results in Fig. 105 are for the reactions between pyridine and benzyl bromide (I) and between triethylamine and

²⁹ Laidler and Eyring, Ref. 1; see also Stearn and Eyring, Ref. 1.

benzyl bromide (II) in alcohol-benzene mixtures; those in Fig. 106 are for the same reactions in benzene-nitrobenzene mixtures.³⁰ From the standpoint of solvent influence, the hydrolysis of an ester may be regarded, at least approximately, as a reaction between two dipoles, the ester and the water molecule; such processes should, therefore, obey Eq. (43). The values of $\log k$ for the hydrolysis of *tert*-butyl chloride (I),³¹ the acid catalyzed hydrolysis of orthoformic ester (III)³² and the alkaline hydrolysis of ethyl benzoate (II)³³ in alcohol-water mixtures are plotted as a function of $(D - 1)/(2D + 1)$ in Fig. 107. The plots in Figs. 105 and 107 are very close to linear in accordance with theoretical requirements, but those for measurements in benzene-nitrobenzene mixtures (Fig. 106) show considerable deviations. It has already been seen that the solvent influence in the Menshutkin reaction can often be correlated with the internal pressure; this implies that the nonelectrostatic forces play an important part, and so it is not justifiable to neglect them, as has been done in the derivation of Eq. (43). The omission of the Φ terms is probably of serious consequence in the Menshutkin reaction because the tertiary amines have only relatively small dipole moments. Thus the approximation made in the deduction of the relationship between $\log k$ and $(D - 1)/(2D + 1)$ is not completely satisfactory, and hence a linear plot is hardly to be expected for the Menshutkin type of reaction.

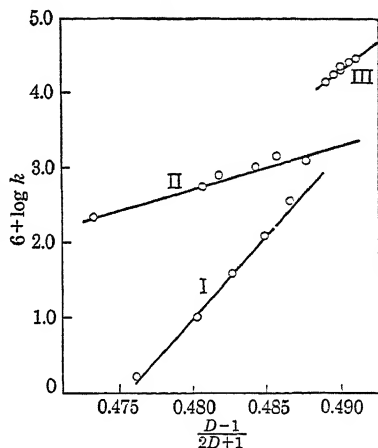


FIG. 107.—Dependence of specific reaction rates on dielectric constant in alcohol-water mixtures.

For solvents such as benzene-nitrobenzene mixtures, which contain a number of small dipoles, the microscopic dielectric

³⁰ G. Muchin, R. Ginsberg and C. Moissejewa, *Ukraine Chem. J.*, **2**, 136 (1926); see *Chem. Zentr.*, **2**, 2376 (1926).

³¹ E. D. Hughes, *J. Chem. Soc.*, 255 (1935).

³² H. S. Harned and N. M. T. Samaras, *J. Am. Chem. Soc.*, **54**, 9 (1932).

³³ R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 538 (1937).

constant may differ from the measured value because of the segregation of one or other of the solvents. Such segregation may also arise because of preferential solubility of reactant or activated complex in one solvent or the other, on account of van der Waals forces. Hence in reactions of the Menschutkin type, the reaction velocity in nitrobenzene may be greater than is to be expected from the dielectric influence of the medium. This is in agreement with the results in Fig. 106 for the formation of quaternary ammonium salts in nitrobenzene-benzene solutions. The effect of benzene may be expected to be in the reverse direction; since the ammonium salt is sparingly soluble in this solvent, the activity coefficient of the activated complex is probably exceptionally large (*cf.* page 406), so that the reaction rate will be lower than is required by Eq. (43). The departure from linearity of the plots in Fig. 106 may thus be explained. Since the small solubility of salts in nonpolar solvents is mainly due to differences in dielectric constant, it is clear that the deviations in benzene solution are due to the neglect of the factors considered above.

Even if Eq. (43) is not quantitatively exact, it may be utilized to indicate qualitatively the influence of solvents in terms of their dielectric constants. The slope of the plot of $\ln k$ against $(D - 1)/(2D + 1)$ is given by

$$\frac{d \ln k}{d[(D - 1)/(2D + 1)]} = -\frac{1}{kT} \left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} \right), \quad (44)$$

and this may be positive or negative, according as the dipole moment of the complex is large or small in comparison with the sum of the moments of the reactants.* For reactions in which the final products are ionized, it is reasonable to suppose that the dipole moment of the complex is large;† and inasmuch as $(D - 1)/(2D + 1)$ increases as the dielectric constant D increases, reactions of this type should be accelerated by solvents of high dielectric constant.

This is in agreement with the results for the rate of formation of quaternary ammonium salts shown in Figs. 105 and 106,

* As a first approximation, $r_{\ddagger}^3 = r_A^3 + r_B^3$; *i.e.*, the volume of the activated complex is equal to the sum of the volumes of the reactants.

† An estimate by A. E. Stearn and H. Eyring [*J. Chem. Phys.*, **5**, 113 (1937)] gives the dipole moment of the complex formed by benzyl bromide and triethylamine as about 6×10^{-18} e.s.u.

and with the general conclusions reached by N. Menshutkin²⁴; as is to be expected, in view of the influence of solvation and of nonelectrostatic forces, the parallelism is not exact. The hydrolysis of esters or alkyl halides yields ionic products; hence, in these instances, increase of reaction rate with increasing dielectric constant of the medium is also to be expected; the results in Fig. 107 confirm this expectation.

It will be realized that it is not always possible to say whether the solvent influence is governed primarily by the van der Waals or by electrostatic forces; if the former is the case, the rate of reaction should be determined mainly by the internal pressure of the medium, but in the latter case the dielectric constant should be the important factor. In many instances, however, the dielectric constant and internal pressure vary in an approximately parallel manner, since for a polar substance both these properties are related to the dipole moment, and a distinction between the two effects cannot be made. In general, polar solvents have high internal pressures and high dielectric constants, and hence such media favor reactions in which the activated complex is more polar than the reactants.

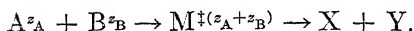
REACTIONS BETWEEN IONS

Dependence on Ionic Strength and Activity Coefficient.—The activity coefficient of an ion in a medium of known ionic strength and dielectric constant depends primarily on its charge; hence by making reasonable assumptions concerning the dimensions of the activated complex formed in a reaction between ions, it is possible to estimate its activity coefficient with greater accuracy than can be achieved in any of the cases already discussed. Two models for the activated complex have been proposed, and at present there seems to be no way of deciding between them; fortunately, however, the conclusions drawn are much the same for both. The two ions involved in a bimolecular reaction are assumed to be spherical; and when they come together to form an activated complex, either the latter can be regarded as retaining the structure of the double sphere, each part carrying its individual charge, or the two spheres may be assumed to merge into one single sphere having a charge equal to the algebraic sum of the two ions concerned. The two types

²⁴ Menshutkin, Ref. 21.

of structure lend themselves to different theoretical treatments, both of which are instructive.

Double-sphere Activated Complex.—The arguments of G. Scatchard,³⁵ using statistical mechanics, are based on the derivation of the Brønsted-Bjerrum equation by J. A. Christiansen³⁶ and may be put in the following form. Consider the reaction between the ions A and B carrying charges z_A and z_B , respectively, which may be positive or negative; the activated complex, designated M^\ddagger , will then carry a charge $z_A + z_B$; thus,



The concentration of activated complex is taken as proportional to the bulk concentration of A ions (c_A) multiplied by the average concentration of B ions (c_B)_{*r*} at a distance *r* from it, where *r* is the distance between A and B in the activated complex. The required concentration of B ions is found by the method of Debye and Hückel to be

$$(c_B)_r = c_B e^{-\psi_r \epsilon z_B / kT}, \quad (45)$$

where c_B is the bulk concentration of B ions, ψ_r is the mean electrostatic potential at a distance *r* from the A ion and ϵ is the unit charge. The concentration of activated complexes is therefore given by

$$c_\ddagger = k' c_A c_B e^{-\psi_r \epsilon z_B / kT}, \quad (46)$$

where k' is the proportionality constant. Upon using the Debye-Hückel expression for ψ_r , this becomes

$$c_\ddagger = k' c_A c_B \exp \left(- \frac{\epsilon^2 z_A z_B}{DkT} \cdot \frac{e^{-\kappa r}}{r} \cdot \frac{e^{\kappa a}}{1 + \kappa a} \right), \quad (47)$$

a being the mean distance of closest approach of the ions. The Debye-Hückel term κ is defined, in the usual manner, by the expression

$$\kappa^2 = \frac{8N\pi\epsilon^2}{1,000 DkT} \mathbf{u} \quad (48)$$

where N is the Avogadro number, and \mathbf{u} is the ionic strength of the medium, *i.e.*, $\frac{1}{2} \sum cz^2$ for all the ions in the solution. When κ

³⁵ G. Scatchard, *J. Am. Chem. Soc.*, **52**, 52 (1930).

³⁶ J. A. Christiansen, *Z. physik. Chem.*, **113**, 35 (1924).

approaches zero, *i.e.*, at high dilution, Eq. (47) becomes

$$c_{\pm}^0 = k' c_A^0 c_B^0 e^{-\varepsilon^2 z_A z_B / DkTr}. \quad (49)$$

By definition, the activity coefficient f is equal to c^0/c , so that

$$\ln \frac{f_A f_B}{f_{\pm}} = \ln \frac{c_A^0 c_B^0}{c_{\pm}^0} - \ln \frac{c_A c_B}{c_{\pm}}; \quad (50)$$

hence, from Eqs. (47) and (49),

$$\ln \frac{f_A f_B}{f_{\pm}} = \frac{\varepsilon^2 z_A z_B}{DkTr} \left(1 - \frac{e^{-\kappa r} \cdot e^{\kappa a}}{1 + \kappa a} \right) \quad (51)$$

$$\approx \frac{\varepsilon^2 z_A z_B}{DkT} \cdot \frac{\kappa}{1 + \kappa a}. \quad (52)$$

For the application of Eq. (6), giving the effect of the medium on the reaction rate, it is necessary to know α , *i.e.*, the activity coefficient in terms of the dilute gas. This is equal to βf , where β is the activity coefficient of an infinitely dilute solution with reference to the ideal gas;* hence,

$$\frac{\alpha_A \alpha_B}{\alpha_{\pm}} = \frac{f_A f_B}{f_{\pm}} \cdot \frac{\beta_A \beta_B}{\beta_{\pm}}. \quad (53)$$

The quantity involving the β terms is given by

$$\ln \frac{\beta_A \beta_B}{\beta_{\pm}} = \ln \frac{c_{\pm}^0}{c_A^0 c_B^0} - \ln \left(\frac{c_{\pm}^0}{c_A^0 c_B^0} \right)_g, \quad (54)$$

the second term on the right-hand side, with the subscript g , being for the ideal-gas state where the dielectric constant is unity. The Debye-Hückel treatment being applied, it follows that

$$\ln \frac{\beta_A \beta_B}{\beta_{\pm}} = \frac{\varepsilon^2 z_A z_B}{kTr} \left(1 - \frac{1}{D} \right), \quad (55)$$

and so it is possible to derive from Eqs. (52), (53) and (55) the value of the α factor in Eq. (6). In this way, it is found that

$$\ln k = \ln k_0 + \frac{\varepsilon^2 z_A z_B}{kTr} \left(1 - \frac{1}{D} \right) + \frac{\varepsilon^2 z_A z_B}{DkT} \cdot \frac{\kappa}{1 + \kappa a}, \quad (56)$$

* The definition for β here differs from that on page 404; but the same symbol is employed, for both quantities are used to relate activity coefficients in solution to those for which the ideal gas is the standard state.

where k_0 is the rate constant in the infinitely dilute, *i.e.*, ideal, gas; this equation should hold, of course, only if all forces other than those of electrostatic origin can be neglected.*

Spherical Activated Complex.—For the spherical activated complex, it is more convenient to adopt a different method of deriving the activity coefficient;³⁷ the principle used is to consider the free energy of transfer of an ion from a medium of dielectric constant unity to that existing in the solution. Suppose the ion is first discharged in a vacuum ($D = 1$); then the free-energy change, according to the method of M. Born³⁸ is equal to $-z^2\epsilon^2/2r$, where r is the radius of the conducting sphere representing the ion on which the charge is assumed to be located. The resulting uncharged radical is then transferred to an infinitely dilute solution, where it experiences an increase of free-energy Φ' due to the van der Waals forces and other forces between it and its neighbors in the solution. The radical is then recharged in the solution of dielectric constant D , when the free-energy change is $z^2\epsilon^2/2rD$. During the recharging process the solvent molecules round the ion will become polarized by the charge and will orient themselves with respect to it; this electrostriction effect will necessitate the introduction of a second non-electrostatic term Φ'' , so that the total free-energy change for the transfer of a single ion from a vacuum, or infinitely dilute gas, to an infinitely dilute solution is

$$\Delta F = -\frac{\epsilon^2 z^2}{2r} + \frac{\epsilon^2 z^2}{2rD} + \Phi_{\beta}' + \Phi_{\beta}''. \quad (57)$$

This quantity is clearly related to the activity coefficient β by the expression $\Delta F = kT \ln \beta$; and so for any ion represented by the subscript i ,

$$\ln \beta_i = \frac{\epsilon^2 z_i^2}{2kTr_i} \left(\frac{1}{D} - 1 \right) + \frac{\Phi_{\beta_i}' + \Phi_{\beta_i}''}{kT}. \quad (58)$$

* The expression in Eq. (56) differs somewhat from the final form given by Scatchard since the latter relates the specific reaction rate in the given solution to that in an infinitely dilute, *i.e.*, ideal, solution in the same solvent.

³⁷ Laidler and Eyring, Ref. 1.

³⁸ M. Born, *Z. Physik*, **1**, 45 (1920).

It follows, therefore, that

$$\ln \frac{\beta_A \beta_B}{\beta_{\ddagger}} = \frac{\varepsilon^2}{2kT} \left(\frac{1}{D} - 1 \right) \left[\frac{z_A^2}{r_A} + \frac{z_B^2}{r_B} - \frac{(z_A + z_B)^2}{r_{\ddagger}} \right] + kT \quad (59)$$

where r_{\ddagger} is the radius of the spherical activated complex and $z_A + z_B$ is its charge. The familiar activity coefficient f , referred to the infinitely dilute solution as the standard state, is given by the ordinary Debye-Hückel treatment, with the addition of a nonelectrostatic term, as

$$\ln f_i = - \frac{\varepsilon^2 z_i^2}{2DkT} \cdot \frac{\kappa}{1 + \kappa a_i} + \frac{\Phi_f}{kT}; \quad (60)$$

hence, if a mean value a is assumed for the distance of closest approach of the various ions, it follows that

$$\ln \frac{f_A f_B}{f_{\ddagger}} = \frac{\varepsilon^2 z_A z_B}{DkT} \cdot \frac{\kappa}{1 + \kappa a} + \frac{\Sigma \Phi_f}{kT}. \quad (61)$$

Upon introducing the value of the expression involving the α terms, derived from Eqs. (59), (61) and (53) into Eq. (6), the result is

$$\ln k = \ln k_0 + \frac{\varepsilon^2}{2kT} \left(\frac{1}{D} - 1 \right) \left[\frac{z_A^2}{r_A} + \frac{z_B^2}{r_B} - \frac{(z_A + z_B)^2}{r_{\ddagger}} \right] + \frac{\varepsilon^2 z_A z_B}{DkT} \cdot \frac{\kappa}{1 + \kappa a} + \frac{\Sigma \Phi}{kT}. \quad (62)$$

If this equation is compared with Eq. (56), based on Scatchard's double-sphere model for the activated complex, it will be seen that, apart from the nonelectrostatic part involving the Φ 's, the only difference is in the second term on the right-hand side of each. This difference is, however, not serious; for if

$$r_A = r_B = r_{\ddagger},$$

the two expressions become identical.

Influence of Ionic Strength.—The equations derived above can be tested in two ways: (1) The dielectric constant may be kept almost constant and the influence observed on the reaction velocity of varying the ionic strength of the medium. (2) The effect on the rate constant extrapolated to zero ionic strength, *i.e.*, at infinite dilution, of changing the dielectric constant may be studied. The first of these problems has been dealt with by

J. N. Brønsted *et al.*,³⁹ using the Brønsted-Bjerrum equation (cf. page 404), thus,

$$k = k_0^s \frac{f_A f_B}{f_{\ddagger}}, \quad (63)$$

where k_0^s is the rate constant for the infinitely dilute solution. If the Debye-Hückel expressions for the activity coefficients are introduced into Eq. (63), then

$$\ln k = \ln k_0^s + \frac{\varepsilon^2 z_A z_B}{DkT} \cdot \frac{\kappa}{1 + \kappa a}. \quad (64)$$

This is the form to which both Eqs. (56) and (62) reduce if the dielectric constant of the medium remains unchanged. Upon inserting the values of κ as given by Eq. (48) and neglecting κa in comparison with unity in the term $1 + \kappa a$, Eq. (64) becomes

$$\ln k = \ln k_0^s + 2A z_A z_B \sqrt{u} \quad (65)$$

where A is a constant for a given solvent and temperature; thus,

$$A = \frac{N^2 \varepsilon^3 (2\pi)^{1/2}}{(DRT)^{3/2} (1,000)^{1/2}}. \quad (66)$$

Upon utilizing the known values of N , ε , D , R and T and introducing the factor for converting natural to ordinary logarithms, A is found to be approximately 0.51* for aqueous solutions at 25°C.; Eq. (65) may, therefore, be written

$$\log k = \log k_0^s + 1.02 z_A z_B \sqrt{u}. \quad (67)$$

It follows from Eq. (67) that the plot of the logarithm of the observed specific reaction rate, *i.e.*, $\log k$, against the square root of the ionic strength of the medium, *i.e.*, \sqrt{u} , should give a straight line of slope $1.02 z_A z_B$; the magnitude and sign of $z_A z_B$ will depend on the nature of the reacting species, and so the slope should vary according to the type of reaction. This theoretical deduction has been amply confirmed for a variety of processes involving positive or negative ions or both. If one of the reactants is a neutral molecule, then $z_A z_B$ should be zero

³⁹ For reviews, see V. K. La Mer, *Chem. Rev.*, **10**, 179 (1932); *J. Franklin Inst.*, **225**, 709 (1938).

* The actual value for an infinitely dilute solution of dielectric constant 78.54 at 25°C. is 0.509.

and the rate constant, at least in dilute solution (*cf.* page 440), should be independent of the ionic strength of the medium; this has also been verified in a number of instances. The experimental results, together with the expected theoretical slope, for reactions of different ionic types are shown in Fig. 108 which is taken from the work of V. K. La Mer.⁴⁰

Deviations from Eq. (67) are observed as the ionic strength of the medium is increased, especially if ions of high valence are

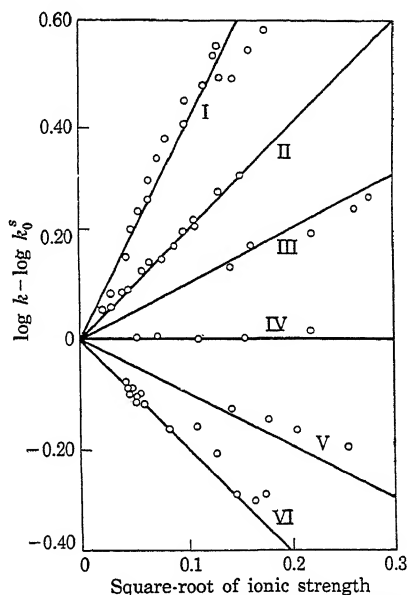


FIG. 108.—Dependence of reaction rates on ionic strength. (La Mer.)

Rate-determining Reaction	$z_A z_B$
I. $\text{Co}(\text{NH}_3)_5\text{Br}^{++} + \text{Hg}^{++}$	+4
II. $\text{S}_2\text{O}_3^{--} + \text{I}^-$	+2
III. $\text{NO}_2\text{:N}\cdot\text{CO}_2\text{C}_2\text{H}_5 + \text{I}^-$	+1
IV. $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{OH}^-$	0
V. $\text{H}_2\text{O}_2 + \text{H}^+ + \text{Br}^-$	-1
VI. $\text{Co}(\text{NH}_3)_5\text{Br}^{++} + \text{OH}^-$	-2

present; this is, of course, to be expected, for in the deduction of the equation the solutions have been assumed to be very dilute. In media of low dielectric constant the formation of associated ions causes marked discrepancies. This has been noted particularly in the reaction between sodium bromacetate

⁴⁰ La Mer, Ref. 39.

and sodium thiosulfate.⁴¹ At very high dilutions, reaction occurs between BrAc^- and $\text{S}_2\text{O}_3^{2-}$ ions, so that $z_A z_B$ is +2; at appreciable concentrations, especially if the dielectric constant is low, the ion complexes $(\text{Na}^+, \text{BrAc}^-)^0$, $(\text{Na}^+, \text{S}_2\text{O}_3^{2-})^-$ and $(2\text{Na}^+, \text{S}_2\text{O}_3^{2-})^0$ are formed and $z_A z_B$ changes to zero. The repulsion between two negatively charged reactants BrAc^- and $\text{S}_2\text{O}_3^{2-}$ is decreased by the formation of the complex ions, and the specific reaction rate is increased at the same time. The very marked catalytic activity of the lanthanum ion on this reaction in aqueous solution is similarly attributed to the fact that the La^{+++} ion enters the activated complex which is now $(\text{BrAc}^-, \text{La}^{+++}, \text{S}_2\text{O}_3^{2-})^0$ instead of $(\text{BrAc}^-, \text{S}_2\text{O}_3^{2-})^-$.⁴²

Influence of Dielectric Constant.—If the ionic strength of the medium is zero, then \sqrt{u} is zero and the terms in Eqs. (56) and (62) involving this quantity disappear; the specific rate constant, extrapolated to zero ionic strength, is thus a function of the dielectric constant at constant temperature. The plot of $\ln k_0$ against $1/D$ should be linear with a slope of

$$\frac{d \ln k_0}{d(1/D)} = - \frac{\varepsilon^2 z_A z_B}{kTr}, \quad (68)$$

according to Eq. (56), and of

$$\frac{d \ln k_0}{d(1/D)} = \frac{\varepsilon^2}{2kT} \left(\frac{z_A^2}{r_A} + \frac{z_B^2}{r_B} - \frac{(z_A + z_B)^2}{r_{\ddagger}} \right) \quad (69)$$

according to Eq. (62). Since r_{\ddagger} , r_A , r_B and r cannot be very different, these two expressions may be regarded as giving results of the same order of magnitude. It is at once apparent from Eq. (68) that if the ions A and B are oppositely charged the slope of the line is positive, whereas it is negative if the ions have the same charge; the same general conclusions may be reached, in a less obvious manner, from Eq. (69). The experimental results are in harmony with the theoretical deductions; by making reasonable assumptions as to the values of the ionic

⁴¹ A. N. Kappanna, *J. Ind. Chem. Soc.*, **6**, 419 (1929); D. Straup and E. J. Cohn, *J. Am. Chem. Soc.*, **57**, 1794 (1935); V. K. La Mer and M. L. Kamner, *ibid.*, **57**, 2669 (1935); S. Eagle and J. C. Warner, *ibid.*, **58**, 2335 (1936); H. M. Tomlinson, Dissertation, Columbia University, 1939.

⁴² V. K. La Mer and M. L. Kamner, *J. Am. Chem. Soc.*, **57**, 2662 (1935); V. K. La Mer, *J. Franklin Inst.*, **225**, 709 (1938).

radii involved, it is possible to calculate by means of Eqs. (68) and (69) the slopes of the plot of $\log k_0$ against $1/D$ which are in excellent agreement with experiment. The most comprehensive studies in this connection have been made with the reaction between bromacetate and thiosulfate ions.⁴³ The results obtained in various aqueous solutions containing urea, glycine and sucrose cover a range of dielectric constant from 20 to 140. The rate constants extrapolated to zero ionic strength are shown by the points in Fig. 109;⁴⁴ the straight line drawn through them corresponds to $r = 5.1 \text{ \AA.}$ in Scatchard's equation. Equally good agreement may be obtained by means of Eq. (69) if the radii of the bromacetate and thiosulfate ions and of the activated complex are taken as 3.3 \AA. , 1.7 \AA. and 5.0 \AA. , respectively. It has been pointed out⁴⁵ that in the deduction of Eq. (56) the activities are taken to be proportional to the volume concentrations, whereas the values given by the theoretical treatment are probably related to the mole fractions. The discrepancy is not serious for dilute solutions in the same solvent, but in comparing the results in different media it may be necessary to make an appropriate allowance. The experimental data for the bromacetate-thiosulfate reaction have been replotted, and a satisfactory straight line is obtained, its slope corresponding to $r = 5.6 \text{ \AA.}$ It is of interest to note that in this plot the rate

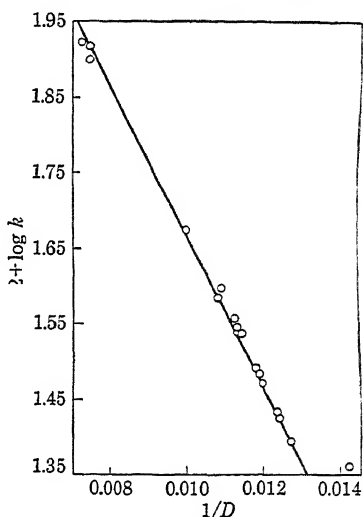


FIG. 109.—Dependence of specific rate of the bromacetate-thiosulfate reaction on dielectric constant of the medium. (La Mer.)

⁴³ V. K. La Mer and R. W. Fessenden, *J. Am. Chem. Soc.*, **54**, 2351 (1932); Straup and Cohn, Ref. 41; La Mer and Kamner, Refs. 41 and 42; Eagle and Warner, Ref. 41; Tomlinson, Ref. 41.

⁴⁴ La Mer, Ref. 42; see also Eagle and Warner, Ref. 41; G. Scatchard, *J. Chem. Phys.*, **7**, 657 (1939).

⁴⁵ Scatchard, Ref. 44.

constant for the reaction in sucrose solution, which is somewhat to the right of the lower end of the straight line in Fig. 109, now falls much closer to the new line; nevertheless, some deviation from the theoretical behavior is not unexpected in a medium of such low dielectric constant, as explained below.

Observations on the reaction between bromphenol blue and hydroxyl ions in mixtures of methyl or ethyl alcohol and water are also in general agreement with expectation from theory.⁴⁶ In this reaction, somewhat different r values, *viz.*, 2.6 and 2.8 Å., respectively, are obtained for the methyl and ethyl alcohol-water mixtures; the significance of this small discrepancy is not clear, but it may be due to the influence of nonelectrostatic forces. The two reactions already considered involve ions of the same sign; the catalytic decomposition of the trimethyl-sulfonium cation by hydroxyl ions⁴⁷ and the combination of ammonium and cyanate ions⁴⁸ involve ions of opposite signs, and the rates of these reactions in media of varying dielectric constant show the expected variation.

Deviations from the straight-line plot of $\log k$ against $1/D$ are frequently found at low dielectric constants; this is probably due to a great extent to the treatment of the solvent as a homogeneous medium of uniform dielectric constant. It is probable that in a mixture of water with a solvent of low dielectric constant the molecules of water will be preferentially oriented around the ions; the dielectric constant in the vicinity of the ion will thus be different from that in the bulk of the medium, which is the value determined experimentally. As long as the solution contains a large proportion of water, the error will not be very significant; but when the dielectric constant is apparently reduced by the addition of a relatively large amount of a solvent of low dielectric constant, the difference between the value in the bulk of the solution and that around the ion will be considerable. The observed reaction velocities at low dielectric constant should thus correspond, as found experimentally, to those for media of higher dielectric constant.

⁴⁶ E. S. Amis and V. K. La Mer, *J. Am. Chem. Soc.*, **61**, 905 (1939).

⁴⁷ J. L. Gleave, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 236 (1935).

⁴⁸ J. C. Warner and E. L. Warrick, *J. Am. Chem. Soc.*, **57**, 1491 (1935); W. J. Svirbely and A. Schramm, *ibid.*, **60**, 330 (1938); J. Lander and W. J. Svirbely, *ibid.*, **60**, 1613 (1938).

Entropy of Activation.—Many reactions in solution have small frequency factors A in the equation $k = A e^{-E_{\text{exp.}}/RT}$; this means either that the standard entropy of activation ΔS^\ddagger has a relatively large negative value or that the transmission coefficient is small. The latter is probably true in a number of instances, but for the present it will be supposed that a “slow” reaction implies a negative entropy of activation. It has been seen in Chap. I that small frequency factors must occur for bimolecular reactions involving fairly complex molecules having a large number of degrees of freedom; values as low as 10^{-5} can be accounted for in this manner. If one of the reactants is a simple ion, however, specific reaction rates that agree, within a factor of 10, with those calculated from the simple collision hypothesis may be expected; this is found to be the case, for example, in the reactions between hydroxyl, phenoxyl and benzoxyl ions and alkyl halides.⁴⁹

When reactions take place between two ions, an important contribution to the entropy of activation arises from electrostatic forces; these give rise to high or low frequency factors according as the charges on the ions are opposite or the same. The quantitative relationship between the magnitude and sign of the charges and the entropy of activation will be considered shortly.

The entropy change accompanying any reversible process may be defined thermodynamically by the equation

$$\Delta S = \left[\frac{\partial(\Delta F)}{\partial T} \right]_p \quad (70)$$

and hence the theoretical deduction of ΔS^\ddagger can be made to depend on a derivation of the corresponding change in the free energy. As seen above, it is only for ionic solutions that anything like a complete theory is available for the calculation of free energies, and even then only for solutions of relatively low concentration. The absolute reaction rate theory equation (see Chap. IV) is

$$k = \frac{kT}{h} e^{-\Delta F^\ddagger/kT}, \quad (71)$$

⁴⁹ Cf. Moelwyn-Hughes, Ref. 5; *Chem. Rev.*, **10**, 241 (1932); G. H. Grant and C. N. Hinshelwood, *J. Chem. Soc.*, 258 (1933).

where ΔF^\ddagger is the standard free energy of activation per molecule; this may be put in the form

$$\ln k = \ln \frac{kT}{h} - \frac{\Delta F^\ddagger}{kT}, \quad (72)$$

the transmission coefficient being taken as unity. Comparison of Scatchard's equation (56) with (72) gives

$$\Delta F^\ddagger = kT \left(\ln \frac{kT}{h} - \ln k_0 \right) - \frac{\varepsilon^2 z_A z_B}{r} \left(1 - \frac{1}{D} \right) - \frac{\varepsilon^2 z_A z_B}{D} \cdot \frac{\kappa}{1 + \kappa a}, \quad (73)$$

and the three terms on the right-hand side may be identified with three types of free-energy changes,⁵⁰ viz., ΔF_0^\ddagger for the ideal gas reaction, ΔF_D^\ddagger as the dielectric effect and ΔF_μ^\ddagger as that due to the Debye-Hückel ionic interactions; thus,

$$\Delta F_0^\ddagger = kT \left(\ln \frac{kT}{h} - \ln k_0 \right), \quad (74)$$

$$\Delta F_D^\ddagger = - \frac{\varepsilon^2 z_A z_B}{r} \left(1 - \frac{1}{D} \right) \quad (75)$$

and

$$\Delta F_\mu^\ddagger = - \frac{\varepsilon^2 z_A z_B}{D} \cdot \frac{\kappa}{1 + \kappa a}. \quad (76)$$

Differentiation of the free-energy term ΔF_D^\ddagger , as expressed by Eq. (75), with respect to temperature, gives

$$\Delta S_D^\ddagger = \frac{\varepsilon^2 z_A z_B}{r D^2} \left(\frac{\partial D}{\partial T} \right)_p, \quad (77)$$

for the dielectric contribution to the entropy of activation at constant ionic strength. In an aqueous medium, D is about 80, and $\partial \ln D / \partial T$ is -0.0046 ; if the distance r is taken as about 2×10^{-8} cm., it is found from Eq. (77) that

$$\Delta S_D^\ddagger \approx -10 z_A z_B \text{ E.U. per mole.} \quad (78)$$

As seen on page 417, $e(kT/h) e^{\Delta S^\ddagger/R}$ is equivalent to the frequency factor A in the equation $k = A e^{-E/RT}$; hence, it follows that, for a reaction between two ions A and B in dilute aqueous

⁵⁰ La Mer and Kamner, Ref. 42; La Mer, Ref. 42; Amis and La Mer, Ref. 46.

solution, the factor A should increase $e^{10/R}$ times, *i.e.*, about one-hundred-fold, for each unit of $-z_A z_B$. The general agreement of this approximate rule with experiment is shown by the results in Table XLIX⁵¹; the column headed "Entropy factor" gives the rough $e^{\Delta S^\ddagger/R}$ values to be expected from this rule, and in the last column are recorded the data obtained from the approximate experimental values of A by means of the relationship between this quantity and $e^{\Delta S^\ddagger/R}$ given above.

TABLE XLIX.—ENTROPY FACTORS IN IONIC REACTIONS

Reaction	$z_A z_B$	Entropy factor	$e^{\Delta S^\ddagger/R}$, (experimental)
$\text{Cr}(\text{H}_2\text{O})_6^{+++} + \text{CNS}^-$	-3	10^6	$\sim 10^5$
$\text{Co}(\text{NH}_3)_5\text{Br}^{++} + \text{OH}^-$	-2	10^4	2×10^4
$\text{NH}_4^+ + \text{CNO}^-$	-1	10^2	0.6
$\text{RH}^+ + \text{Cl}^-$	-1	10^2	0.8
$\text{ClO}^- + \text{ClO}_2^-$	1	10^{-2}	4×10^{-5}
$\text{C}_6\text{H}_5\text{C}\equiv\text{C}\cdot\text{COO}^- + \text{I}_3^-$	1	10^{-2}	7×10^{-6}
$\text{CH}_2\text{Cl}\cdot\text{COO}^- + \text{S}_2\text{O}_3^{--}$	2	10^{-4}	6×10^{-7}
$\text{Co}(\text{NH}_3)_5\text{Br}^{++} + \text{Hg}^{++}$	4	10^{-8}	6×10^{-6}
$\text{AsO}_3^{--} + \text{TeO}_4^{--}$	6	10^{-12}	$\sim 10^{-7}$

If the medium is supposed to remain unchanged, then differentiation of Eq. (76), for ΔF_μ^\ddagger , with respect to temperature gives

$$\Delta S_\mu^\ddagger = \frac{\Delta F_\mu^\ddagger}{T} \left(\frac{3}{2} \cdot \frac{\partial \ln D}{\partial \ln T} + \frac{1}{2} \cdot \frac{\partial \ln V}{\partial \ln T} + \frac{1}{2} \right) \quad (79)$$

for the entropy of activation resulting from ionic interaction. Upon neglecting the term involving the variation of the volume V of the solution with temperature and inserting the value of $\partial \ln D / \partial \ln T$, *i.e.*, -1.37 at 25°C., for water, it follows that

$$\Delta S_\mu^\ddagger = -1.55 \frac{\Delta F_\mu^\ddagger}{m} \quad (80)$$

If κa in Eq. (76) is neglected, *i.e.*, for a dilute solution, and the value of κ as given by Eq. (48) is inserted, the result is

$$\frac{\Delta F_\mu^\ddagger}{2.3RT} = -1.02 z_A z_B \sqrt{\mu} \quad (81)$$

⁵¹ For references, see Moelwyn-Hughes, Ref. 5, Chap. VII; see also *idem*, *Proc. Roy. Soc.*, **155**, A, 308, 1936.

so that

$$\frac{\Delta S_{\mu}^{\ddagger}}{2.3R} = 1.58z_A z_B \sqrt{u}. \quad (82)$$

For media of constant dielectric constant,

$$\Delta S^{\ddagger} = \Delta S_0^{\ddagger} + \Delta S_{\mu}^{\ddagger}, \quad (83)$$

since ΔS_D^{\ddagger} is zero; hence,

$$\frac{\Delta S^{\ddagger} - \Delta S_0^{\ddagger}}{2.3R} = 1.58z_A z_B \sqrt{u}. \quad (84)$$

and so the plot of $\Delta S^{\ddagger}/2.3R$ against \sqrt{u} should be a straight line of slope $1.58z_A z_B$, provided that the solutions are not too concentrated. Since the frequency factor A is equal to

$$e \left(\frac{kT}{h} \right) e^{\Delta S^{\ddagger}/R},$$

as already seen, it follows that $\log A$ is equal to $\Delta S^{\ddagger}/2.3R$ plus a constant term; the plot of $\log A$ against \sqrt{u} should thus satisfy the conditions derived above. Measurements on the rate of the reaction between bromphenol blue and hydroxyl ions in aqueous solution have given results in agreement with expectation.⁵²

If the medium is so adjusted that the dielectric constant does not vary with temperature, it follows from Eq. (77) that ΔS_D^{\ddagger} will be zero; if the results so obtained are extrapolated to zero ionic strength, $\Delta S_{\mu}^{\ddagger}$ will also be zero. The total entropy of activation should thus be equal to ΔS_0^{\ddagger} for the ideal reaction and hence should be independent of the constant value of the dielectric constant of the medium. This expectation has been confirmed experimentally.

Heats of Activation.⁵³—If the thermodynamic relationship $\Delta H = \Delta F + T \Delta S$ is utilized, it follows from Eqs. (75) and (77) that for media of constant ionic strength the contribution of the

⁵² Amis and La Mer, Ref. 46.

⁵³ W. J. Svirbely and J. C. Warner, *J. Am. Chem. Soc.*, **57**, 1883 (1935); Svirbely and Schramm, Ref. 48; Lander and Svirbely, Ref. 48; L. O. Winstrom and J. C. Warner, *ibid.*, **61**, 1205 (1939); La Mer, Ref. 42; J. C. Warner, *Ann. New York Acad. Sci.*, **39**, 345 (1940).

dielectric effect to the heat of activation is

$$\Delta H_{D^{\ddagger}} = -\frac{\varepsilon^2 z_A z_B}{rD} + \frac{\varepsilon^2 z_A z_B}{rD^2} \left(1 + T \frac{\partial D}{\partial T} \right). \quad (85)$$

If in addition to maintaining the ionic strength constant the medium is varied so as to keep the dielectric constant independent of temperature, *i.e.*, if $\partial D/\partial T$ is zero, it follows that

$$(\Delta H_{D^{\ddagger}})_D = -\frac{\varepsilon^2 z_A z_B}{rD} + \frac{\varepsilon^2 z_A z_B}{rD^2}, \quad (86)$$

and hence

$$\Delta H_{D^{\ddagger}} - (\Delta H_{D^{\ddagger}})_D = T \frac{\varepsilon^2 z_A z_B}{rD^2} \cdot \frac{\partial D}{\partial T}. \quad (87)$$

For reactions in solution, ΔH^{\ddagger} is related to the experimental activation energy by the equation $E_{\text{exp.}} = \Delta H^{\ddagger} + RT$ (*cf.* page 199), and so Eq. (87) should give the difference between the experimental activation energies in a medium of fixed composition and one of fixed dielectric constant. The relationship has been found to be in agreement with the results of measurements on the conversion of ammonium cyanate into urea in various solvents.

It can be readily derived from Eq. (76) that, for a medium of constant composition,

$$\Delta H_{\mu^{\ddagger}} = \Delta F_{\mu^{\ddagger}} \left[\frac{3}{2} \cdot \frac{\partial \ln D}{\partial \ln T} + \frac{1}{2} \cdot \frac{\partial \ln V}{\partial \ln T} + \frac{3}{2} \right] \quad (88)$$

giving the contribution of ionic interaction to the heat of activation. If the $\partial \ln V/\partial \ln T$ term is neglected, as before, and the value of $\partial \ln D/\partial \ln T$ given above is inserted, it follows that, for an aqueous solution at 25°C.,

$$\Delta H_{\mu^{\ddagger}} = -0.55 \Delta F_{\mu^{\ddagger}}, \quad (89)$$

and hence, from Eq. (81),

$$\frac{\Delta H_{\mu^{\ddagger}}}{2.3RT} = 0.56 z_A z_B \sqrt{u}. \quad (90)$$

The total heat of activation ΔH^{\ddagger} is the sum of ΔH_0^{\ddagger} for the ideal reaction, $\Delta H_{D^{\ddagger}}$ for the dielectric effect and $\Delta H_{\mu^{\ddagger}}$ which is under consideration; for a medium of constant dielectric

constant, ΔH_D^\ddagger , as given by Eq. (86), is constant and hence it is seen that

$$\Delta H^\ddagger = \text{const.} + \Delta H_\mu^\ddagger, \quad (91)$$

since ΔH_0^\ddagger is also constant. It follows, consequently, from Eqs. (90) and (91) that the plot of the experimental activation energy, equal to $\Delta H^\ddagger + RT$, against the square root of the ionic strength, for media of constant dielectric constant, should be a straight line of slope $2.3RT \times 0.56z_A z_B$, for aqueous solutions at 25°C. For nonaqueous solutions the linear relationship between $E_{\text{exp.}}$ and \sqrt{u} should still be found, but the slope should depend on the nature of the solvent. The theoretical deductions are here, also, in agreement with experiment.

Finally, consideration will be given to the variation of ΔH^\ddagger as a function of dielectric constant at zero ionic strength. It has been seen that, if the dielectric constant is maintained independent of temperature, ΔS_D^\ddagger is zero; under these conditions, therefore, ΔH_D^\ddagger is equal to ΔF_D^\ddagger . Further, at zero ionic strength, ΔH_μ^\ddagger is zero; hence,

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \Delta H_D^\ddagger + \Delta H_\mu^\ddagger \quad (92)$$

$$= \Delta H_0^\ddagger + \Delta F_D^\ddagger. \quad (93)$$

$$\Delta H^\ddagger - \Delta H_0^\ddagger = - \varepsilon^2 z_A z_B \left(1 - \frac{1}{D} \right). \quad (94)$$

The experimental activation energy should thus depend on the dielectric constant of the medium in the manner indicated by Eq. (94), and this expectation has also been confirmed by measurements on the isomerization of ammonium cyanate in methyl alcohol-water mixtures.

Attention may be called to the fact that according to Eq. (67) the rate of reaction between two ions of the same sign will increase with increasing ionic strength, at constant dielectric constant, although it is seen from Eq. (90) that the energy of activation also increases under the same conditions. This result provides an illustration of one of the fundamental bases of the theory of absolute reaction rates, *viz.*, that the velocity of a reaction is determined primarily by the *free energy*, not by the heat, of activation (page 196). It will be seen from Eq. (73) that for a reaction between ions of the same sign the free energy of activa-

tion decreases with increasing ionic strength of the medium, and hence the rate of reaction increases. The increase in entropy more than outweighs the increase in heat of activation, and so the net result is a decrease of free energy.

REACTIONS BETWEEN IONS AND NEUTRAL MOLECULES

Influence of Ionic Strength and Dielectric Constant.⁵⁴—If one of the reactants, *e.g.*, B, is a neutral molecule, its charge is zero; *i.e.*, $z_B = 0$. Equation (56) is then no longer applicable, but according to (62) a straight line of slope

$$\frac{d \ln k}{d(1/D)} = \frac{\varepsilon^2 z_A^2}{2kT} \left(\frac{1}{r_A} - \frac{1}{r_+} \right) \quad (95)$$

should be obtained for the plot of $\ln k$ against $1/D$. Since r_+ will, as a general rule, be greater than r_A , the slope will be positive, so that the rate of reaction between an ion and a neutral molecule should decrease with increasing dielectric constant of the medium. Examples of this type of behavior are to be found in the reactions between alkyl halides and hydroxyl⁵⁵ or halide ions⁵⁶ and between water and a sulfonium cation.⁵⁷

According to Eq. (67) a reaction involving an ion and a neutral molecule should not be affected by the ionic strength of the medium; it will be clear from the deduction, however, that this can be true only provided that the solutions are dilute. At appreciable concentrations a definite dependence of the rate constant on the ionic strength is observed experimentally, and the theoretical relationship may be derived in the following manner. In writing the value of $\ln \alpha$ it is necessary to include, in addition to the factors $\ln \beta$ and $\ln f$, as given by Eqs. (55) and (52), and the nonelectrostatic contribution $\Sigma \Phi/kT$, the additional electrostatic term $b_{\mathbf{u}}$, introduced by E. Hückel,⁵⁸ which becomes appreciable at high salt concentrations. In the final equation for an ion and a neutral molecule the other electro-

⁵⁴ Laidler and Eyring, Ref. 1.

⁵⁵ C. A. Lobry de Bruyn and A. Steger, *Rec. trav. chim.*, **18**, 41, 311 (1899); E. D. Hughes, C. K. Ingold and U. G. Shapiro, *J. Chem. Soc.*, 225 (1936).

⁵⁶ E. Bergmann, M. Polanyi and A. Szábo, *Z. physik. Chem.*, **B**, **20**, 161 (1933); F. Juliusburger, B. Topley and J. Weiss, *J. Chem. Phys.*, **3**, 437 (1935).

⁵⁷ E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1571 (1933).

⁵⁸ E. Hückel, *Physik. Z.*, **26**, 93 (1925).

static terms cancel, and the Hückel term is the only one involving the ionic strength of the medium that is left. It is at once apparent, therefore, why it must be included in the treatment of concentrated solutions. The complete expression for $\ln \alpha_A$ for the ionic reactant A is now written [see Eqs. (58) and (60)]

$$\ln \alpha_A = \frac{\varepsilon^2 z_A^2}{2r_A kT} \left(\frac{1}{D} - 1 \right) - \frac{\varepsilon^2 z_A^2}{2DkT} \cdot \frac{\kappa}{1 + \kappa a} + b_A \psi + \frac{\Phi_A}{kT}, \quad (96)$$

and a similar equation holds for the activity coefficient of the activated complex which has the same charge as A.

The activity coefficient of the neutral molecule B is obtained by considering the free energy of transfer of an uncharged particle from the vapor to a medium of dielectric constant D_0 which is that of the solution containing the substance B, but in which no ions are yet present. This is given by the Kirkwood equation (25), modified by the introduction of nonelectrostatic terms, as

$$\Delta F = - \frac{\mu_B^2}{r_B^3} \cdot \frac{D_0 - 1}{2D_0 + 1} + \frac{\Phi'_B}{kT}. \quad (97)$$

The next step is to determine the free-energy change resulting from the introduction of the ions into the solution of nonelectrolyte; this is given by the approximate expression of P. Debye and J. McAulay⁵⁹ which relates the free energy of the process to the change of the dielectric constant of the solvent resulting from the addition of the nonelectrolyte: thus,

$$\Delta F = \frac{\varepsilon^2 \delta}{2D} \sum \frac{n_i z_i^2}{r_i} \quad (98)$$

where n_i is the number of ions per cubic centimeter of the i th kind, of radius r_i and valence z_i ; δ is defined by

$$D = D_0(1 - \delta n_B), \quad (99)$$

where D_0 is the dielectric constant of the pure solvent and D is that of the solution containing n_B molecules of nonelectrolyte per cubic centimeter. The activity coefficient of B, obtained from the relationship $\Delta F = kT \ln \alpha_B$, is then given by

$$\ln \alpha_B = - \frac{1}{kT} \cdot \frac{\mu_B^2}{r_B^3} \cdot \frac{D_0 - 1}{2D_0 + 1} + \frac{1}{kT} \cdot \frac{\varepsilon^2 \delta}{2D} \sum_i \frac{n_i z_i^2}{r_i}. \quad (100)$$

⁵⁹ P. Debye and J. McAulay, *ibid.*, 26, 22 (1925).

Upon introducing the values of $\ln \alpha_A$ and $\ln \alpha_{\ddagger}$, as given by (96), and of $\ln \alpha_B$ [Eq. (100)] in Eq. (6), it follows that

$$\ln k = \ln k_0 + \frac{\varepsilon^2 z_A^2}{2kT} \left(\frac{1}{D} - 1 \right) \left(\frac{1}{r_A} - \frac{1}{r_{\ddagger}} \right) - \frac{1}{kT} \cdot \frac{\mu_B^2}{r_B^3} \cdot \frac{D_0 - 1}{2D_0 + 1} \\ + \left(b_A - b_{\ddagger} + \frac{\varepsilon^2 \delta}{DrkT} \right) \mathbf{u} + \frac{\sum \Phi}{kT}. \quad (101)$$

The Debye-Hückel term involving $\kappa/(1 + \kappa a)$ has been eliminated by the assumption that the mean distance of closest approach a is the same for the A ions and the activated complex, and a value r is used for the mean of the r_i terms in Eq. (100). It is seen from Eq. (101) that, provided the dielectric constant is unchanged, $\log k$ at appreciable concentrations should vary in a linear manner with the ionic strength, instead of with its square root as for reactions involving two ions. The work of J. N. Brønsted and W. F. K. Wynne-Jones⁶⁰ on the hydrolysis of acetals by hydrogen ions confirms this deduction.

If the Kirkwood and electrostatic terms are small, then, for a medium of definite dielectric constant, Eq. (101) may be written

$$\ln k = \ln k_D + b\mathbf{u}. \quad (102)$$

$$\therefore k = k_D e^{b\mathbf{u}}, \quad (103)$$

where b is equal to $b_A + b_M - b_{\ddagger}$, the quantity b_M representing the Debye-McAulay correction $\varepsilon^2 \delta / DrkT$. If $b\mathbf{u}$ is small, then all terms involving powers of b higher than the first may be neglected in the expansion of the exponential, so that Eq. (103) reduces to

$$k = k_D(1 + b\mathbf{u}). \quad (104)$$

Under these conditions the plot of k , instead of $\log k$, against \mathbf{u} should be a straight line; this has been found to be the case in the hydrolysis of ethylene acetal and other acetals and of several esters, in the hydration of ethylene oxide and in the decomposition of diazoacetic ester.⁶¹

Before considering other aspects of reactions in solution it will be opportune to summarize here the effect of dielectric constant and of ionic strength on reactions of various types;

⁶⁰ J. N. Brønsted and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

⁶¹ Cf. J. N. Brønsted and C. Grove, *J. Am. Chem. Soc.*, **52**, 1394 (1930).

the results of the theoretical treatment of the present chapter are given in Table L.⁶²

TABLE L.—INFLUENCE OF DIELECTRIC CONSTANT AND IONIC STRENGTH ON REACTIONS OF DIFFERENT TYPES

Reaction type	Effect of increasing		Examples
	Dielectric constant	Ionic strength	
I. Two dipolar molecules forming a polar product.	Increase	No effect	$R_3N + RX$ $H_2O + RX$ Hydrolysis of esters
II. Two ions: a. Same sign.	Increase	Increase	$BrAc^- + S_2O_3^{--}$ $OH^- +$ brom-phenol blue
b. Opposite sign.	Decrease	Increase	$OH^- + Me_3S^+$
III. Ion and neutral molecule.	Decrease	Increase	$OH^- + RX$ $OR^- + RX$ $X^- + RX$ $Me_2BuS^+ + H_2O$

THE DENATURATION OF PROTEINS⁶³

Heat and Free Energy of Activation.—One of the most interesting applications of the theory of absolute reaction rates is in connection with the problem of the denaturation of proteins and the inactivation of certain enzymes. The temperature coefficients of the reaction rates are often very large, leading to energies of activation of 100 kcal. or more; in spite of these exceptionally high values, the reactions occur with appreciable velocities at ordinary temperatures. Further, the experimental activation energies frequently vary markedly with pH, and in certain instances, *e.g.*, denaturation of egg albumin by concentrated urea solution, the energy of activation is apparently negative. Many of these apparent difficulties can be removed by determining the free energies of activation of the reactions;

⁶² For data, see refs. 55, 56 and 57; also, D. P. Evans and H. O. Jenkins, *Trans. Faraday Soc.*, **36**, 818 (1940).

⁶³ Stearn and Eyring, Ref. 1; A. E. Stearn, *Ergebnisse Enzymforsch.*, **7**, 1 (1938); H. Eyring and A. E. Stearn, *Chem. Rev.*, **24**, 253 (1939).

this is done by utilizing the experimental specific reaction rate (k) in conjunction with Eq. (71) of the theory of absolute reaction rates. The heat of activation ΔH^\ddagger can be derived from the plot of $\ln k/(kT/h)$ against $1/T$ [cf. Eq. (158), page 196]. It is then possible to obtain the value of ΔS^\ddagger by means of the familiar thermodynamic relationship. The results obtained in this manner from measurements at about 50°C. on the inactivation of yeast invertase at different pH's are quoted in Table LI.⁶⁴

TABLE LI.—INACTIVATION OF INVERTASE AT 50°C.

k , sec. ⁻¹	pH	ΔH^\ddagger , kcal.	ΔS^\ddagger , e.u.	ΔF^\ddagger , kcal.
7.7×10^{-5}	5.7	52.35	84.7	25.0
50×10^{-5}	5.2	86.35	185.0	25.7
3.5×10^{-5}	4.0	110.35	262.5	25.5
3.75×10^{-5}	3.0	74.35	152.4	24.4

It is seen that in spite of the variation of ΔH^\ddagger between 52 and 110 kcal., the free energy of activation remains almost constant. Further, it will be observed that the exceptionally high energies of activation are compensated to a very great extent by large increases of entropy accompanying activation. The result is that ΔF^\ddagger is relatively small; hence, according to the theory of absolute reaction rates, the reaction will be rapid at ordinary temperatures, in spite of the high heat of activation. Attention may be called in passing to the fact that with increasing pH both ΔH^\ddagger and ΔS^\ddagger pass through maxima at a pH of about 4.0; this matter will be considered more fully later.

A further illustration of the essential importance of the free energy, rather than the heat of activation, is to be found in connection with the inactivation and reactivation of trypsin. From the observed velocities at pH 6.5, the value of ΔH^\ddagger was found to be 40 kcal.⁶⁵; but from measurement of the equilibrium constants at pH 2 to 3, ΔH for the whole reaction appears to be 67.7 kcal.⁶⁶ Unless the change in ΔH^\ddagger due to pH exceeds 27.6 kcal., these results mean that the energy of activation of an endothermic reaction is less than the heat absorbed in the

⁶⁴ Data from H. von Euler and I. Lauren, *Z. physiol. Chem.*, **108**, 64 (1919).

⁶⁵ J. Pace, *Biochem. J.*, **24**, 606 (1930).

⁶⁶ M. L. Anson and A. E. Mirsky, *J. Gen. Physiol.*, **17**, 393 (1934).

reaction; in that case the energy of activation of the reverse process, *i.e.*, the reactivation, should be negative! In spite of this, however, the reverse reaction is slower than the forward reaction, although the ΔH^\ddagger of the latter is much larger. The explanation of these results is to be found in the fact that the entropy of activation for the reverse reaction has a large negative value, so that ΔF^\ddagger is about 27 kcal., in spite of the negative value of ΔH^\ddagger .

The occurrence of high heats of activation accompanied by large increases of entropy, leading to free energies of activation in the range of 20 to 30 kcal., is very common in connection with the denaturation of proteins and inactivation of enzymes, especially in regions of pH close to that of maximum stability. This fact is brought out by the data in Table LII for a variety of substances.

TABLE LII.—DENATURATION OF PROTEINS AND INACTIVATION OF ENZYMES

Reactant	Catalyst	pH	ΔH^\ddagger , kcal.	ΔS^\ddagger , E.U.	ΔF^\ddagger , kcal.
Egg albumin.....	Water	5.0	132.1	315.7	25.4
Hemoglobin.....	Water	6.8	76.3	152.0	24.5
Hemoglobin.....	3 <i>N</i> (NH ₄) ₂ SO ₄	6.76	119.8	275.8	25.2
Pepsin.....	6.44	55.6	113.3	21.9
Rennin.....	89.3	208.1	22.1
Trypsin.....	6.5	40.2	44.7	25.7

Although ΔH^\ddagger for the denaturation of egg albumin is as high as 130 kcal. at pH's of 5.0 to 7.7, it is only 35 kcal. in acid solutions of pH 1 to 1.7 at 25°C. The entropies of activation are also correspondingly less, so that the free energy of activation is still about 24 kcal. Similar results have been recorded for the denaturation of hemoglobin.

Significance of Entropy of Activation.—The explanation of the high entropies of activation and their dependence on pH is said to lie in the existence of salt bridges, formed between acidic and basic groups, in the native protein, which are broken on denaturation. At the pH of maximum stability the number of such bridges is believed to be a maximum, and the protein has a very restricted configuration. As a result of heating or of the addition of small amounts of acid or alkali, the bridges are

broken, and the resulting loosening of the structure must be accompanied by a large increase of entropy. If the loosening has already occurred, to some extent, in the activated state, there will be a large entropy of activation, as found experimentally. In very acid solutions, the salt bridges will be broken spontaneously as a result of the neutralization of the basic groups of the protein; the entropy of activation for the denaturation process, as measured by the influence of temperature on the reaction rate, will thus be small under these conditions. The free energy of activation is not greatly dependent on the pH of the solution, and so ΔH^\ddagger changes in accordance with the variation of ΔS^\ddagger . It can be seen, in general, that ΔH^\ddagger and ΔS^\ddagger should be a maximum at the pH of maximum stability of the protein and should fall off on either side; this is in agreement with the results in Table I.I.

Another way of considering the problem is to realize that salt bridges may be broken either by neutralization resulting from a change of pH or by the supply of energy; in the former case, most of the heat change is treated as the heat of neutralization and does not appear in the measured ΔH^\ddagger , but in the latter the heat involved is the difference between the strength of the salt-bridge bonds and that of any bonds formed subsequently with the solvent. In aqueous solutions, particularly if salts are present, there is virtually no interaction between the broken bonds and the solvent, and hence the value of ΔH^\ddagger will be high, especially in the region of pH of maximum stability. On the other hand in urea solutions there is considerable combination between the urea and the free bonds of the protein; and if the heat evolved in this process is greater than that required to break the salt bridges, the heat of activation will be negative, as has sometimes been observed. In these circumstances, since the activated complex is even more restricted than the native protein, the entropy of activation is a large negative quantity.

The argument that breaking salt, and other, bridges is accompanied by an increase of entropy which offsets to a great extent the corresponding heat change must not be taken to imply that all bridges contribute to the entropy increase on breaking. If the first bridges broken resulted in a considerable loosening of the structure, and hence a large entropy increase, the free

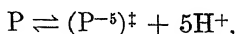
energy of activation would be so small that the denaturation process would occur with extreme rapidity; in fact, denaturation, under these conditions, would be spontaneous, and native protein would be unknown. It appears, therefore, that the process of activation consists in the breaking of those bridges which are not accompanied by much increase of entropy; those that do make an appreciable positive contribution in this respect will break spontaneously. The unusual fact, recorded above, that, for the inactivation of trypsin, ΔH for the equilibrium exceeds ΔH^\ddagger for the activation process means that after activation many bonds open spontaneously; the large positive value of $T \Delta S^\ddagger$ is now presumably greater than the corresponding ΔH^\ddagger , and so this part of the denaturation process is very rapid. It is seen, therefore, that although there may be a further increase of heat content in going from the activated to the final state, as observed, the free energy may be decreased owing to the large gain of entropy.*

Choice of Standard States.—It was stated above that the recorded values of ΔH^\ddagger and ΔS^\ddagger , and to some extent ΔF^\ddagger , for the denaturation of proteins and inactivation of enzymes vary with the pH of the solution; since these thermodynamic quantities refer to changes with the reactants and the activated complex in their standard states, the result is perhaps somewhat surprising. The difficulty lies in the fact that variable standard states are being chosen, particularly with reference to the hydrogen ion, for this is usually taken as the concentration, or activity, in the reacting system. The specific reaction rate of any process is only a constant, at definite temperature and pressure, provided that the rate equation includes the activities of all substances which take part in the equilibrium between initial and activated states. These statements may be illustrated by reference to the studies of the deactivation of pepsin; from experiments made in media of constant pH, it was found that the reaction rate is proportional to the pepsin concentration and *inversely* proportional to the fifth power of the hydrogen-ion concentration.⁶⁷

*The correctness of these theoretical considerations is independent of possible uncertainties in the particular experimental results quoted.

⁶⁷ J. Steinhardt, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **14** [11] (1937); *Nature*, **138**, 74 (1936); see also V. K. La Mer, *Science*, **86**, 614 (1937).

This means (*cf.* page 190) that the activated complex contains five protons less than the normal state, so that the equilibrium, if the water is disregarded, is to be represented by



where P is the active pepsin and $(P^{-5})^{\ddagger}$ is the activated complex which contains five protons less than P. According to the discussion on page 402 the velocity of reaction (v) is given by

$$v = K^{\ddagger} \frac{a_P}{a_{H^{+}}^5} \cdot \frac{kT}{h}, \quad (105)$$

where K^{\ddagger} is written for $K_0^{\ddagger}/\alpha_{\ddagger}$. If the pepsin is regarded as the only reactant, the specific rate is

$$k' = \frac{K^{\ddagger}}{a_{H^{+}}^5} \cdot \frac{kT}{h}, \quad (106)$$

so that it appears to be inversely proportional to the fifth power of the hydrogen-ion activity. To obtain a true constant, however, it is necessary to take both the pepsin and the hydrogen ions in their standard states; the specific rate is then

$$k = k' a_{H^{+}}^5 = K^{\ddagger} \frac{kT}{h}. \quad (107)$$

If the values of the specific rate obtained by this procedure were utilized to derive ΔH^{\ddagger} , ΔS^{\ddagger} and ΔF^{\ddagger} , in the usual manner, the results would be found to be independent of the pH of the medium, apart from extraneous effects due to the variation of ionic strength or dielectric constant.

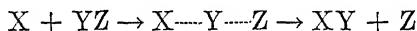
INFLUENCE OF SUBSTITUENTS ON REACTION VELOCITY⁶⁸

Effect on Activation Energy.—It is well known that in many simple reactions with organic compounds, *e.g.*, hydrolysis, alcoholysis, esterification, bromination, etc., the introduction of substituents into the molecule of reactant produces definite changes in reaction velocity which can frequently be correlated with the electronic properties of the substituent group. The changes in the specific rate are sometimes accompanied by changes in the energy of activation, and if the substituent is

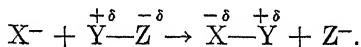
⁶⁸ C. N. Hinshelwood, K. J. Laidler and E. W. Timm, *J. Chem. Soc.*, 848 (1938).

near the point of reaction in the molecule there are often variations in the frequency factor. In several instances a parallelism has been observed between the changes in the two quantities⁶⁹ which, in a sense, is similar to the connection between heat and entropy of activation noted in other cases.⁷⁰ It is possible, however, that the changes in bond strength resulting from the introduction of various substituents affect the energy of activation; there will, at the same time, be small changes in the vibrational frequencies which affect the partition functions in the absolute-reaction-rate equation.

Apart from the influence of substituents on the frequency factor, their effect on activation energies is more clearly understood, and the problem has been approached from several angles. It was seen in Chap. III that the activation energy for a reaction of the type



depends on four factors: (1) the strength of the bond between Y and Z; (2) the repulsion between X and YZ; (3) the repulsion between XY and Z and (4) the strength of the bond between X and Y. Suppose that by introducing a substituent into the molecule YZ the repulsion between X and YZ is decreased and the attraction between Y and Z is increased; this may be imagined as happening if X is a negative ion, or the negative portion of a dipolar molecule, and the substituent has the effect of increasing the positive charge on Y and the negative charge on Z, thus:



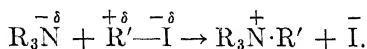
As a result of this substitution the four factors that determine the energy of activation will be altered; the increase in the strength of the Y—Z bond will tend to increase the energy of activation,* whereas the decreased repulsion between X and

⁶⁹ R. A. Fairclough and C. N. Hinshelwood, *ibid.*, 538, 1573 (1937); E. W. Timm and C. N. Hinshelwood, *ibid.*, 862 (1938).

⁷⁰ See Evans and Polanyi, Ref. 11; Bell, Ref. 11; I. M. Barclay and J. A. V. Butler, *Trans. Faraday Soc.*, **34**, 1445 (1938).

* For this particular reaction, in which Z comes off as an ion, it is the ionic character, or ionizability, of the Y—Z bond, rather than its strength, which is important.

YZ, and between XY and Z, and the increased strength of the X—Y bond, which is a consequence of the decreased repulsion between X and Y, will all tend to lower the activation energy. Any increase in the latter is thus due to the predominating effect of the attraction of the reactant X for YZ, and the importance of this factor is shown by the experimental proof that in the majority of reactions studied the influence of a substituent on the energy of activation is in the direction to be expected from its effect on the attraction of the reagent to the seat of the reaction (see also page 459). The formation of quaternary ammonium salts provides an example of this type of behavior. The results in Table LIII are for the activation energies of the reactions between triethylamine or pyridine, representing the reactant X, and methyl, ethyl or isopropyl iodide, representing YZ, in benzene solution; thus,



The figures show a pronounced rise in the activation energy as the number of methyl groups substituted in the iodide is increased.⁷¹

TABLE LIII.—ACTIVATION ENERGIES FOR THE FORMATION OF QUATERNARY AMMONIUM SALTS

Amine	Iodide	$E_{\text{exp.}}$, kcal.
Triethylamine.....	Methyl	9.7
	Ethyl	11.4
	Isopropyl	17.1
Pyridine.....	Methyl	14.3
	Ethyl	15.8
	Isopropyl	18.0

The observed results are attributed to the positive inductive, *i.e.*, electron-repelling, effect of the methyl groups, so that as the alkyl radical becomes more complex the charge on the carbon atom which attracts the approaching base is made more negative, *i.e.*, less positive. In accordance with the discussion above, this change should be accompanied by an increase of activation energy.

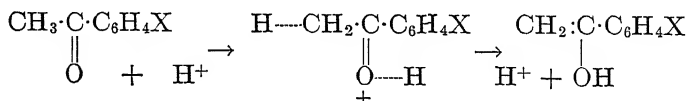
⁷¹ C. A. Winkler and C. N. Hinshelwood, *J. Chem. Soc.*, 1147 (1935); K. J. Laidler and C. N. Hinshelwood, *ibid.*, 858 (1938).

Influence of Repulsion.—In passing from the weak base pyridine to the stronger base triethylamine, the attraction for the same alkyl iodide increases and the activation energy is seen to be decreased. The influence on the activation energy of the strength of the base, which is related to the negative charge on the nitrogen atom, is brought out clearly by the results in Table LIV for the reaction between methyl iodide and a series of substituted dimethylanilines in nitrobenzene solution. The order of the substituents gives that of increasing negative inductive effects and consequently of gradual weakening of the base, accompanied by a decreasing negative charge on the nitrogen and hence a diminished attraction for the alkyl iodide.⁷²

TABLE LIV.—ACTIVATION ENERGIES FOR REACTION BETWEEN METHYL IODIDE AND SUBSTITUTED DIMETHYLANILINES

Substituent	$E_{\text{exp.}}$, kcal.
<i>p</i> -OCH ₃	11.7
<i>p</i> -CH ₃	12.3
(H)	12.8
<i>p</i> -Br	13.7
<i>p</i> -Cl	13.9

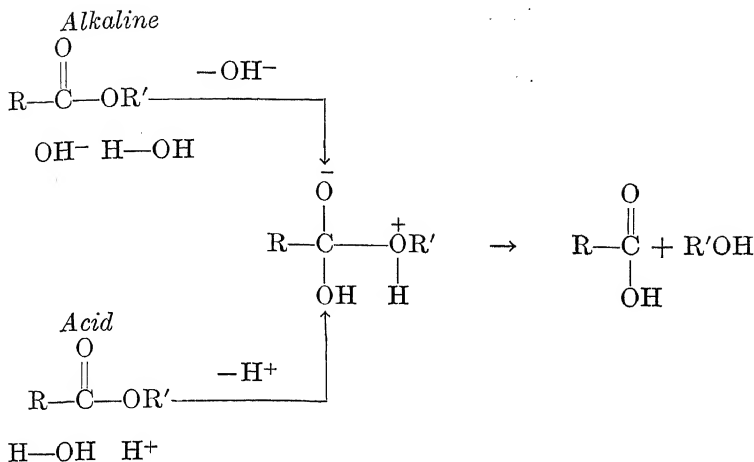
The change in repulsion between X and YZ, due to alteration of the attraction between Y and Z brought about by a substituent in YZ, is apparently important in certain catalyzed prototropic changes. For example, the activation energies in the prototropic changes of substituted acetophenones



vary in the direction determined by the attraction of the catalyzing proton, although this is the direction of increasing strength of attachment of the mobile hydrogen atom.⁷³ Benzene substitution generally follows the same rule, for the ease with which the hydrogen atom goes off appears to be of little importance. A similar situation exists in the hydrolysis of esters, although the mechanism is here more complicated. The alkaline and acid hydrolysis may be represented as follows:

⁷² K. J. Laidler, *ibid.*, 1786 (1938); cf. D. P. Evans, H. B. Watson and L. Williams, *ibid.*, 1345 (1939).

⁷³ D. P. Evans, V. G. Morgan and H. B. Watson, *ibid.*, 1167 (1935).



The effect of a substituent in the acidic, *i.e.*, R, group of the ester on the activation energy is in the same direction in each case,⁷⁴ showing that the charge on the carbonyl carbon atom operates in the same way in both types of hydrolysis. In alkaline hydrolysis the charged ion attacks this carbon atom, where the effect is less. In acid hydrolysis, however, it is the uncharged water molecule that attacks the carbonyl carbon atom, and the proton attaches itself to the oxygen atom of the OR' group. The repulsion terms are undoubtedly different in the two cases; the activation energies are thus found to differ—by about 5 to 7 kcal.—in spite of the fact that the same bonds are formed in each case. Bearing in mind that the attraction and repulsion due to an ion will be considerably greater than that of a water molecule, it is possible to construct the following table showing the change in activation energy to be expected when a group with a negative inductive effect, *e.g.*, NO₂, is introduced into the radical R of the ester.

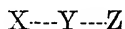
Approach of	Alkaline	Acid
(1) OH ⁻ to C (of CO group)...	Marked decrease
(2) H ₂ O to O (of OR group)...	Increase
(3) H ⁺ to O (of OR group)...	Increase
(4) H ₂ O to C (of CO group)...	Decrease

⁷⁴ C. K. Ingold and W. S. Nathan, *ibid.*, 222 (1936); E. W. Timm and C. N. Hinshelwood, *ibid.*, 862 (1938).

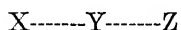
On balance, the effect of the substituent would be expected to be greater in alkaline than in acid hydrolysis. This is in agreement with the fact that the influence of substituents is known to be very much more marked in alkaline hydrolysis. In acid hydrolysis the effect of (4) would probably outweigh that of (3) when a substituent is introduced into the R group, and so a small decrease in the activation energy is to be anticipated if the substituent is one with a negative inductive effect.

Influence of Bond Strength or Ionic Character.—When the attraction between X and Y is relatively small, *i.e.*, when the repulsion is large, the energy of activation will no longer be determined primarily by the repulsion energy between X and YZ; the strength, or ionizability, of the Y—Z bond will now play an important part. This point may be illustrated by the data in Table LIII; it has been seen that as the attraction between the nitrogen of an amine and the carbon atom of an alkyl group is diminished, by the introduction of methyl groups into the latter, the activation energy increases. It will be observed, further, that when the halide is isopropyl iodide and the attraction is small, the activation energy is almost the same for reaction with either pyridine or triethylamine. Although there is a difference of 4.6 kcal. for the interaction of methyl iodide with these two bases in benzene solution, this is reduced to less than 1.0 kcal. for the isopropyl iodide. Similar results have been obtained in nitrobenzene solution where the difference in activation energies for isopropyl iodide and the same two bases is about 0.7 kcal.

In general terms, it can be seen that, if the repulsion between X and YZ is relatively large, it may require less energy to extend the YZ bond than to force X right up to Y. The two possible activated complexes may be represented as



for the first case, when X is forced up to Y, and



for the second, when the bond YZ is extended; the potential energy of the latter configuration is smaller than that of the former. For the reactions under consideration the atom or radical Z comes off as an ion; therefore, it is probably the ionic

character of the Y—Z bond, rather than its strength, that is the determining factor. In cases of this kind the influence of substituents on the reaction velocity will depend on their effect on the strength or ionizability of the Y—Z bond; as seen on page 448, the introduction of groups that strengthen this bond, or decrease its ionic character, increases the activation energy, and therefore in these circumstances the influence of substituents will be in the opposite direction to that observed when the repulsion between X and YZ is the dominant factor. The existence of this effect may be seen by comparing the results in Table LV for the alcoholysis of acyl chlorides with those for the alcoholysis of the corresponding triarylmethyl chlorides, both in methyl alcohol solution.⁷⁵

TABLE LV.—ACTIVATION ENERGIES OF ALCOHOLYTIC REACTIONS

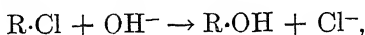
Acyl chloride	$E_{\text{exp.}}$, kcal.	Triarylmethyl chloride	$E_{\text{exp.}}$, kcal.
$p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{Cl}$	11.10	$(p\text{-NO}_2\cdot\text{C}_6\text{H}_5)_3\text{C}\cdot\text{Cl}$	16.71
$p\text{-Cl}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{Cl}$	13.85	$(p\text{-Cl}\cdot\text{C}_6\text{H}_5)_3\text{C}\cdot\text{Cl}$	13.48
$\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{Cl}$	14.40	$(\text{C}_6\text{H}_5)_3\text{C}\cdot\text{Cl}$	13.42
$p\text{-CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{Cl}$	18.65	$(p\text{-CH}_3\text{O}\cdot\text{C}_6\text{H}_4)_3\text{C}\cdot\text{Cl}$	12.45

In the alcoholysis of the acyl chloride the introduction of a negative, *i.e.*, electron-attracting, group diminishes the repulsion of the hydroxyl group of the approaching alcohol molecule, while causing the chlorine to ionize less readily; the fact that the energy is lowered shows that the change in the repulsive energy is the more important. In the other reactions, however, the effect of substituents is in the opposite direction, the energy of activation decreasing as the ionic character of the C—Cl bond is increased. The difference in behavior in the two cases lies, apparently, in the larger positive charge carried by the carbonyl carbon atom than by the carbon atom of the triphenylmethyl chloride, because of the attachment of the former to an oxygen atom. The attraction for the approaching group is large in the former case and small in the latter. In accordance with the arguments already developed, therefore, the change in repulsive energy will deter-

⁷⁵ G. E. K. Branch and A. C. Nixon, *J. Am. Chem. Soc.*, **58**, 2499 (1936); A. C. Nixon and G. E. K. Branch, *ibid.*, **58**, 492 (1936).

mine the energy of activation in the reaction with the acyl chloride but the alteration of the strength or, more correctly, the ionizability of the C—Cl bond will be the determining factor in the triphenylmethyl chloride reactions.

The interaction between alkyl halides and hydroxyl or alkoxy ions provides an interesting illustration of what is probably an intermediate type of behavior, for the effects of repulsion and bond strength appear to cancel each other. In the reaction

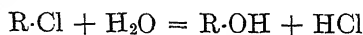


for example, the change of R from methyl through ethyl to isopropyl should increase the activation energy if repulsion has the dominating influence (*cf.* page 449); but if the ionic character of the C—Cl bond were the determining factor, the change in activation energy should be in the opposite direction. It will be seen from Table LVI that for a number of reactions of this type the energy of activation is almost the same for the three halides.⁷⁶

TABLE LVI.—ACTIVATION ENERGIES OF ALKYL HALIDE REACTIONS

Reaction	R = Methyl, kcal.	Ethyl, kcal.	Isopropyl, kcal.
$\text{R}\cdot\text{Cl} + \text{OH}^-$	23.00	23.00
$\text{R}\cdot\text{Br} + \text{OH}^-$	21.00	21.70
$\text{R}\cdot\text{I} + \text{C}_6\text{H}_5\cdot\text{O}^-$	22.12	22.00	22.10
$\text{R}\cdot\text{I} + \text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{O}^-$	20.57	21.86	21.41

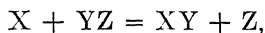
If the reactant were a water molecule instead of a negative ion, the repulsion effect should be larger, since the latter exerts a greater attraction on the carbon atom of the alkyl halide than does the neutral water molecule. If the two factors under consideration, *viz.*, repulsion between the reactants and the ionizability of the C—Cl bond, balance almost exactly in the reaction with hydroxyl ions, then in reactions of the type



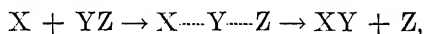
⁷⁶ Grant and Hinshelwood, *Ref.* 49; Hughes, Ingold and Shapiro, *Ref.* 55; K. A. Cooper and E. D. Hughes, *J. Chem. Soc.*, 1138 (1937); see also D. Segaller, *ibid.*, 103, 1421 (1913); 105, 106 (1914); P. C. Haywood, *ibid.*, 121, 1904 (1922).

the nature of the change in the ionic character of the C—Cl bond should determine the direction of the change in activation energy. Increasing the number of methyl groups, *i.e.*, increasing the positive inductive effect, in the R radical will increase the ionizability of the C—Cl bond and so should diminish the activation energy for the reaction of the halide with water. This is in agreement with experiment, for isopropyl and *tert*-butyl halides are much more readily hydrolyzed by water than are the corresponding methyl or ethyl halides.⁷⁷ The results recorded in Table LV which showed that the reaction between triarylmethyl chloride, *i.e.*, a substituted alkyl chloride, and alcohol, *i.e.*, a substituted water, is governed by the bond strength, are consequently in harmony with these conclusions.

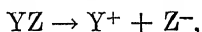
The point of view considered here is essentially similar to that adopted by E. D. Hughes and C. K. Ingold⁷⁸ for the discussion of reactions of the type



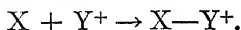
where X is a nucleophilic reagent.* It is suggested that two mechanisms are possible; the first, designated by S_N2 , is bimolecular and takes place thus,



whereas the second S_N1 is unimolecular, the slow stage being ionization of YZ by the breaking of the Y—Z bond, thus,



followed by the rapid reaction



Intermediate cases have been observed and instances have been found in which the change from the S_N2 to the S_N1 type occurs as the number of substituent alkyl groups is increased, *e.g.*, in the hydrolysis of alkyl halides. It is evident that the two schemes of Hughes and Ingold are analogous to the two types of cases considered above; in the S_N2 type of reaction the repul-

⁷⁷ Cf. E. D. Hughes, *ibid.*, 255 (1935).

⁷⁸ E. D. Hughes and C. K. Ingold, *ibid.*, 244 (1935); see also E. D. Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938).

* A nucleophilic reagent is one that transfers to or shares electrons with a foreign nucleus; bases and reducing agents are nucleophilic in character.

sion energy is the important factor, whereas in the S_N1 type it is the ionizability of the Y—Z bond that determines the activation energy. The arguments for one point of view may, therefore, be used equally for the other.

Activation Energy and Dipole Moment.—In reactions such that the energy of activation is affected directly by the electron-attracting or -repelling influence of substituent groups, it is to be expected that there should be some connection between the activation energy and the dipole moment, or other electrical property, of the substituent. Such a relationship has been proposed by W. A. Waters⁷⁹ and by H. B. Watson and his collaborators⁸⁰ in the form of the equation

$$E = E_0 - c(\mu + b\mu^2), \quad (108)$$

where E_0 is the activation energy for a given reaction with the unsubstituted molecule and E is that for the substituted molecule; μ is the dipole moment of the substituent group, and b and c are constants. This expression has been found to hold reasonably well for m -substituents in the acid-catalyzed prototropic change of acetophenone, in the alkaline hydrolysis of benzoic esters and in the benzylation of aromatic amines. In some cases, where measurements have been made at one temperature only, a similar correlation has been found between $\log k$ and μ ; if the frequency factor is the same for a given series of reactions, this is equivalent to a relationship between the activation energy and the dipole moment of the substituent.⁸¹

It has been pointed out that, since the dipole moment is a vector quantity, it cannot be altogether satisfactory to connect the activation energy with the actual moment without taking into account the direction in which the latter operates. The proposal has been made⁸² to consider, instead of μ , the electrostatic potential produced by the substituent group at the carbon atom to which the reacting center is attached. If r is the

⁷⁹ W. A. Waters, *Phil. Mag.*, **8**, 436 (1938).

⁸⁰ W. S. Nathan and H. B. Watson, *J. Chem. Soc.*, 893 (1933); J. F. J. Dippy and H. B. Watson, *Chem. and Ind.*, **54**, 735 (1935); *J. Chem. Soc.*, 436 (1936).

⁸¹ D. P. Evans, V. G. Morgan and H. B. Watson, *ibid.*, 1174 (1936); E. G. Williams and C. N. Hinshelwood, *ibid.*, 1079 (1934); see also Nathan and Watson, Ref. 80.

⁸² H. O. Jenkins, *J. Chem. Soc.*, **640**, 1137, 1780 (1939).

distance between this carbon atom and the point of operation of the dipole of the substituent and θ is the angle between the line joining these two points and the direction of the dipole, then the electrical potential, which is a measure of the work done in bringing a unit charge from infinity up to the carbon atom, is defined by

$$\psi = \frac{\mu}{r^2} \cos \theta. \quad (109)$$

If the electrostatic potentials obtained in this way are plotted against the activation energies for the alkaline hydrolysis of substituted benzoic esters, the benzoylation of substituted amines and the formation of quaternary ammonium salts, the results fall almost exactly on a straight line. The slope of this line for the first reaction is almost identical with the magnitude of the charge carried by a mole of hydroxyl ions, and hence it is concluded that the change in the energy of activation is almost entirely accounted for by the work done in bringing up the hydroxyl ion against the field produced at the point of reaction by the dipole of the substituent group. In a number of instances, *e.g.*, the hydrogen-ion catalyzed esterification of substituted benzoic acids, the hydrolysis of substituted benzyl halides and the reaction of the latter with potassium iodide, a similar connection exists between the potential and the logarithm of the specific reaction rate. If the frequency factor is approximately the same for all the reactions in any one series, as is probable, this means that the linear relationship between ψ and E is also applicable in these cases.

In some reactions the behavior of *o*- and *p*-compounds is exceptional; this may be attributed in the latter instance to the time-variable electromeric effect which does not reveal itself in the dipole moment, for it exists only in the activated complex. Another disturbing factor is that the mesomeric effect, which should be included in the measured dipole moment, is frequently changed by the presence of other groups in the benzene nucleus.⁸³ The abnormality of *o*-compounds has been much discussed, but the situation is still by no means clear.⁸⁴

⁸³ G. M. Bennett and S. Glasstone, *Proc. Roy. Soc.*, **145**, A, 71 (1934).

⁸⁴ For reviews, see H. B. Watson, "Modern Theories of Organic Chemistry," p. 205, Oxford University Press, 1937; *Ann. Rep. Chem. Soc.*, **35**, 243 (1938).

Rates of Ortho-, Meta-, and Para-substitution.⁸⁵—It is generally agreed that the operation of the positive inductive and resonance (electromeric) effects of a substituent in a benzene ring makes the electron density on the *o*- and *p*-carbon atoms greater than on the *m*-atom; the result is that electrophilic reagents will tend to react in the *o*- and *p*-positions, rather than in the *m*-position. By making a number of simple postulates, it has been found possible to calculate the distribution of charges, and hence the dipole moment, in the molecule from the ratio of the amounts of *o*-, *m*- and *p*-products obtained in nitration. Further, in the reverse calculation the relative amounts of *o*-, *m*- and *p*-nitro compounds have been derived from the dipole moments. The assumptions, which appear reasonable, are:

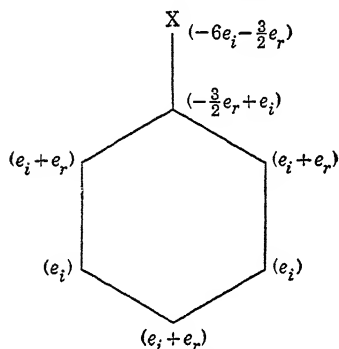


FIG. 110.—Distribution of charges in benzene derivative. (Ri and Eyring.)

the carbon atom to which it is attached. The charge distribution will thus be represented by Fig. 110; since e_i may be identified with e_m , the charge in the *m*-position, it follows that

$$e_o = e_p = e_m + e_r, \quad (110)$$

where $e_m = e_i$, and

$$e_1 = e_m - \frac{3}{2}(e_p - e_m), \quad (111)$$

$$e_x = -6e_m - \frac{3}{2}(e_p - e_m), \quad (112)$$

where e_x and e_1 are the charges on the substituent X and on the carbon atom to which it is attached, respectively.

When an electrophilic reagent, with an effective charge e_n , approaches any carbon atom Y which is acting as a center of

⁸⁵ T. Ri and H. Eyring, *J. Chem. Phys.*, **8**, 433 (1940).

reaction, then the electrostatic interaction is equal to $e_y e_n / rD$, where e_y is the charge on the carbon atom, r is the distance of separation of the charges and D is the dielectric constant of the medium between them. If ΔF^\ddagger is the free energy of activation of the process in the absence of any electrostatic effects, then it is reasonable to suppose that as a consequence of the attraction between the charges e_n and e_y the free energy of activation will be reduced* to $\Delta F^\ddagger + e_y e_n / rD$, where r and D now refer to the activated state. There is much evidence for the view that the effective agent in nitration reactions is the ion NO_2^+ , and hence the charge e_n of the reagent may be taken as equal to the unit electronic charge 4.8×10^{-10} e.s.u. Since in the activated state the NO_2^+ ion must approach very closely to the carbon atom at which reaction occurs, the value of r will not be very different from the normal $\text{C}-\text{NO}_2$ distance; the latter is 1.46 Å., but r will be taken as 1.6 Å., for in an activated complex there is generally an extension of about 10 per cent over the equilibrium interatomic distances. Finally, it is necessary to consider the magnitude of the dielectric constant of the medium between the charges; it is evident that, in view of the very close approach of the charges in the activated state, this cannot be related in any way to the dielectric constant of the solvent. This anticipation is supported by the fact that the ratios of the amounts of *o*-, *m*- and *p*-forms produced in nitration are generally independent of the nature of the solvent used.⁸⁶ Since there is no actual matter between the charges of the reagent and of the carbon atom acting as reaction center when the activated state is formed, it is reasonable that D may be taken as unity.

According to the theory of absolute reaction rates, the transmission coefficient being omitted, the specific rate is given by

$$k_y = \frac{kT}{h} e^{-(\Delta F^\ddagger + e_y e_n / rD) / kT}; \quad (113)$$

but in order to make use of this relationship it is necessary to know something of ΔF^\ddagger , the free energy of activation in the absence of electrostatic effects. If the assumption is made

* This is a reduction, in spite of the positive sign, because e_n is a positive and e_y a negative quantity in this example.

⁸⁶ Cf. M. L. Bird and C. K. Ingold, *J. Chem. Soc.*, 918 (1938); G. A. Benford and C. K. Ingold, *ibid.*, 929 (1938).

that for the nitration, or other substitution reaction, of benzene the charge e_y represents the difference between the charge on the carbon atom in the presence and absence of the group X, so that e_y is zero for benzene itself, it follows that

$$k_E = \frac{kT}{-} e^{-\Delta F^\ddagger/kT}. \quad (114)$$

where k_H is the specific rate of the nitration at any given carbon atom for benzene itself. Combination of Eqs. (113) and (114) gives the ratio of relative specific rates for any carbon atom as

$$\frac{k_y}{k_H} = e^{-e_y e_n / r D k T}. \quad (115)$$

Since the molecule $C_6H_5 \cdot X$ under consideration has two *o*-, two *m*- and one *p*-positions, whereas benzene has six identical positions, it follows that the ratios of the actual velocities (v) under similar conditions of *o*-, *m*- and *p*-substitution, as compared with benzene, are given by

$$\frac{v_o}{v_H} = \frac{1}{3} \cdot \frac{k_o}{k_H} = \frac{1}{3} e^{-e_o e_n / r D k T}, \quad (116a)$$

$$\frac{v_m}{v_H} = \frac{1}{3} \cdot \frac{k_m}{k_H} = \frac{1}{3} e^{-e_m e_n / r D k T}, \quad (116b)$$

$$\frac{v_p}{v_H} = \frac{1}{6} \cdot \frac{k_p}{k_H} = \frac{1}{6} e^{-e_p e_n / r D k T}. \quad (116c)$$

The ratio v_o/v_H gives the relative amounts of nitration in the *o*-position of $C_6H_5 \cdot X$ and of benzene in a competitive reaction. Suppose a_X and a_H represent the total amounts, *i.e.*, *o*, *m* and *p*, of $C_6H_5 \cdot X$ and of benzene, respectively, nitrated in a given time, and x_o is the fraction of the former which is in the *o*-form; then it follows that

$$\frac{v_o}{v_H} = x_o \frac{a_X}{a_H}, \quad (117)$$

and hence, by (116a) and (117),

$$\frac{k_o}{k_H} = 3x_o \frac{a_X}{a_H} = e^{-e_o e_n / r D k T}. \quad (118)$$

Similarly, for the *m*- and *p*-reactions,

$$\frac{k_m}{k_H} = 3x_m \frac{a_X}{a_H} = e^{-e_m e_n / r D k T}, \quad (119a)$$

and

$$\frac{k_p}{k_H} = 6x_p \frac{a_X}{a_H} = e^{-e_p e_n / r D k T}. \quad (119b)$$

It is seen, therefore, that from the proportions, *viz.*, x_o , x_m and x_n , of *o*-, *m*- and *p*-compounds formed in the nitration of $C_6H_5 \cdot X$ and the ratio of the amounts, *i.e.*, a_X/a_H , obtained in the competitive nitration of $C_6H_5 \cdot X$ and benzene, it should be possible to calculate e_o , e_m and e_p . From these the values of e_i and e_r , the individual charges due to induction and resonance, can be estimated by means of Eqs. (110), (111) and (112), and hence the complete charge distribution in the $C_6H_5 \cdot X$ molecule may be determined (*cf.* Fig. 110).

The accuracy of the distribution of charges derived in this manner may be tested by calculating the dipole moment of the molecule $C_6H_5 \cdot X$. If r_x is the distance from X to the adjacent carbon atom and r_b is the distance from the latter to any point, chosen for convenience as O , the center of the ring (Fig. 111), then it follows that the dipole moment is given by

$$\mu = e_x(r_x + r_b) + e_1 r_b + 2e_o(\frac{1}{2}r_b) - 2e_m(\frac{1}{2}r_b) - e_p r_b, \quad (120)$$

where the first and second terms give the contributions of the group X and the carbon atom to which it is attached and the others represent the moments along the X— C_6H_5 axis due to the charges on the two *o*-, two *m*- and one *p*-carbon atoms, respectively. Cancellation of terms in Eq. (120) gives

$$= e_x(r_b + r_x) + (e_1 - e_m)r_b, \quad (121)$$

and so μ can be readily calculated from e_x , e_1 and e_m and the known interatomic distances.

There appear to be two substances only, *viz.*, toluene and ethyl benzoate, for which competitive nitrations have been performed in the presence of benzene and for which the amounts

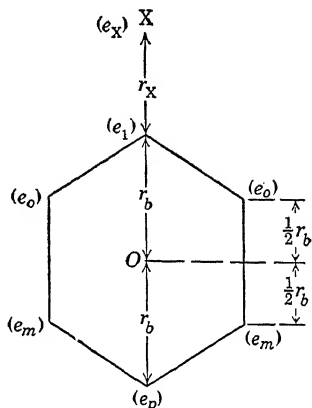


FIG. 111.—Calculation of dipole moment of benzene derivative from charge distribution. (*Ri and Eyring.*)

of *m*-compound obtained on nitration were sufficient to be determined with any degree of accuracy. There are many instances, however, where such small quantities of the *m*-substituent were isolated that the extent of substitution in this position has been taken as zero; this is not strictly true, however, and there is evidence that in some instances 0.3 per cent of *m*-product is obtained.⁸⁷ For the purpose of the calculations, the results of which are given below, a proportion of 0.2 per cent has been assumed throughout.* The charge distribution in a number of compounds, obtained by means of Eqs. (118), (119a) and (119b), and the corresponding dipole moments, derived from (121), are given in Table LVII; they were obtained, as explained above, from measurements on the rates of nitration and the amounts of nitro compounds in competitive nitration with benzene.

TABLE LVII.—CHARGE DISTRIBUTION IN BENZENE DERIVATIVES IN 10^{-10} E.S.U.

	X = CH ₃	CO·OC ₂ H ₅	F	Cl	Br	I
e_o	(-0.0491)	(0.0776)	(0.0363)	(0.0473)	(0.0446)	(0.0194)
e_m	-0.0128	0.0649	0.0933	0.115	0.116	0.0909
e_p	-0.0532	0.0950	0.0035	0.0271	0.0305	0.0065
e_1	0.0478	0.0198	0.181	0.247	0.244	0.218
e_z	0.137	-0.430	-0.473	-0.558	-0.568	-0.419
μ (calc.)	0.48	-1.31*	-1.20	-1.54	-1.68	-1.27 D.
μ (obs.)	0.44	-1.91	-1.45	-1.55	-1.53	-1.30 D.

* The discrepancy between the calculated and observed results arises here because the method employed gives essentially the dipole moment of the bond adjacent to the benzene ring. When allowance is made for the whole ester group, as in Table LVIII, the agreement is much better.

It will be noted that different values are recorded for e_o and e_p , whereas the simple theory requires them to be the same; the latter neglects, however, the effect on the *o*-position of the proximity of the carbon atom to which the substituent X is attached. For the purpose of calculating the dipole moment, e_p was employed to give $e_i + e_r$; but if e_o had been used, the results

⁸⁷ A. F. Hollemann "Die direkte Einführung von Substituenten in den Benzolkern," Leipzig, 1910.

* In the majority of cases, it is reported that within an experimental error of 0.2 per cent no *m*-product is obtained; the proportion of 0.2 per cent has been assumed here arbitrarily because it leads to satisfactory results.

would differ from those in Table LVII by no more than 5 per cent.

For those substances for which competitive nitration in the presence of benzene has not been carried out, an alternative procedure may be adopted to determine the charge distribution. If (119*b*) is divided by (119*a*), it follows that

$$2 \frac{x_p}{x_m} = e^{-(e_p - e_m)e_n/rDkT}, \quad (122)$$

or

$$kT \ln \frac{2x_p}{x_m} = - \frac{(e_p - e_m)e_n}{rD}; \quad (123)$$

hence, if e_m can be obtained from other considerations, e_p could be calculated from a knowledge of the ratio of *p*- and *m*-compounds produced in nitration. The assumption is made, therefore, that the inductive contribution to the dipole moment of a monosubstituted benzene is equal to the moment $\mu_{\text{ali.}}$ ⁸⁸ of the corresponding tertiary aliphatic compound, so that

$$\mu_{\text{ali.}} = -6e_i(r_b + r_x) = -6e_m(r_b + r_x), \quad (124)$$

and hence e_m may be readily calculated. The charge distributions and dipole moments obtained in this manner are recorded in Table LVIII.

TABLE LVIII.—CHARGE DISTRIBUTION IN BENZENE DERIVATIVES IN 10^{-10} E.S.U.

	X = NO ₂	COOH	CO-OCH ₃	CO-OC ₂ H ₅	CH ₂ Cl	CHCl ₂	CCl ₃ *
e_o	(0.263)	(0.0594)	(0.1062)	(0.1125)	(0.083)	(0.122)	(0.118)
e_m	(0.191)	0.0411	0.0929	0.101	0.114	0.117	0.0876
e_p	0.248	0.0871	0.123	0.131	0.070	0.104	0.0892
e_1	0.105	-0.0342	0.0473	0.0562	0.180	0.136	0.0900
e_x	-1.23	-0.316	-0.603	-0.653	-0.617	-0.683	-0.524
μ (calc.)	-3.63	-1.02	-1.83	-1.98	-1.69	-1.95	-1.41 D.
μ (obs.)	-3.81	-1.00	-1.86	-1.91	-1.82	-2.04	-2.11 D.

* These results are based on $\mu_{\text{ali.}}$ for methyl chloroform, which may account for the unsatisfactory value of μ (calc.).

Calculation of Relative Amounts of Substituents.—Since dipole moments of monosubstituted benzenes can be calculated with fair accuracy from a knowledge of the moments of the correspond-

⁸⁸ Cf. L. E. Sutton, *Proc. Roy. Soc.*, **133**, A, 668 (1931).

ing *tert*-butyl compounds, *i.e.*, μ_{ali} , and the proportions of *o*-, *m*- and *p*-compounds produced in nitration, it should evidently be possible to reverse the procedure. If the values of e_1 and e_x given by Eqs. (111) and (112), respectively, are inserted in (121), it follows that

$$\mu_{\text{aro.}} = -6e_m(r_b + r_x) - \frac{3}{2}(e_p - e_m)(r_x + 2r_b); \quad (125)$$

hence, if μ_{ali} and $\mu_{\text{aro.}}$ are known, it is possible to calculate e_p and e_m by means of Eqs. (124) and (125). A knowledge of these quantities leads directly to an evaluation of x_p/x_m by means of (122). An analogous equation, in which e_o replaces e_m , gives x_o/x_m , and so the ratio of *o*-, *m*- and *p*-forms can be derived. It is evident that if the same values were used for e_p and e_o as the simple theory requires, the amounts of *o*- and *p*-compounds would be the same; this is known to be incorrect, and the reason, as indicated above, is the interaction between the *o*-carbon atom and the adjacent one to which the substituent X is attached. The correct value of e_o to be used in the calculation is obtained by the empirical relationship

$$e_o = e_p + \frac{e_1 - e_p}{15}; \quad (126)$$

this gives values for e_o very close to those in Tables LVII and LVIII. The proportions of *o*-, *m*- and *p*-forms to be expected in the nitration of nitro-, chloro-, bromo- and iodo-benzenes have been calculated in this manner; the results are in good agreement with those observed,¹ as is to be expected in view of the satisfactory values for the dipole moments obtained in the reverse calculation.

INFLUENCE OF EXTERNAL PARAMETERS ON REACTION VELOCITY

General Treatment.⁸⁹—The general case of the effect of external parameters, of which the change of a substituent is a special instance, may be considered from another aspect. According to the theory of absolute reaction rates

$$k = \kappa \frac{kT}{h} e^{-\Delta F^\ddagger/RT}; \quad (127)$$

⁸⁹ M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935); **32**, 1333 (1936); M. G. Evans, *ibid.*, **34**, 49 (1938).

and so, at constant temperature, it is possible to write

$$\ln k = \text{const.} - \frac{\Delta F^\ddagger}{RT}, \quad (128)$$

the transmission coefficient κ also being regarded as remaining constant. This equation may be written in the form

$$\ln k = \text{const.} - \frac{1}{RT} \left[\frac{\partial(\Delta F^\ddagger)}{\partial \chi} \right]_\tau d\chi, \quad (129)$$

where χ is some continuous parameter representing an intensity factor such as pressure or electric field strength, the assumption being made that $\partial(\Delta F^\ddagger)/\partial \chi$ remains constant over a range of this parameter. Writing g^\ddagger as an abbreviation for the quantity $\partial(\Delta F^\ddagger)/\partial \chi$, which gives the effect of χ on the free energy of activation, (129) becomes

$$\ln k = \text{const.} - \frac{g^\ddagger}{RT} d\chi. \quad (130)$$

Influence of Substituents.—Imagine a series of reactions, designated by the superscript A, in which the various processes are fundamentally the same except that there is a change in the group substituted in one of the reactions; the parameter χ which may represent the electrostatic field at the reaction center, will have a series of special values $\chi_1^A, \chi_2^A, \chi_3^A \dots \chi_i^A$, etc. It follows, therefore, that for the reaction of type A, Eq. (130) can be written in the form

$$\ln k_i^A = \text{const.} - \frac{g_A^\ddagger}{RT} d\chi_i^A. \quad (131)$$

Consider another group of reactions, indicated by B, and suppose the same changes are made as in the previous case by introducing substituents; the appropriate form of (130) is then

$$\ln k_i^B = \text{const.} - \frac{g_B^\ddagger}{RT} d\chi_i^B. \quad (132)$$

If the two groups of reactions are not very different in type, *e.g.*, they may both depend on the approach of an ion or polar part of a molecule of the same sign, then $d\chi_i^A/d\chi_i^B$ is likely to be the same for all the substituents; in many cases, it may, of

course, be equal to or very close to unity. Replacing this ratio by a constant C , it follows from Eqs. (131) and (132) that

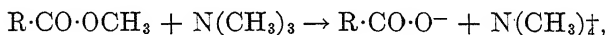
$$\ln k_i^A = C \frac{g_B^\ddagger}{g_A^\ddagger} \ln k_i^B + \text{const.} \quad (133)$$

If, as has been supposed, the two reactions A and B are fundamentally similar, the influence of the parameter χ_A on the activation free energy of reactions of the type A, *i.e.*, g_A^\ddagger , will be related in a definite manner to the influence of χ_B on the free energy of activation of the B reactions; $g_B^\ddagger/g_A^\ddagger$ may thus be taken as constant, so that Eq. (133) becomes

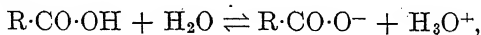
$$\log k_i^A = x \log k_i^B + \text{const.}, \quad (134)$$

where x is a constant for the given two groups of reactions. This equation should relate the influence of a series of substituents on the rate of a given reaction A to that of the same substituents on the rate of a related process B.

Rate Constants and Equilibrium Constants.—Instead of comparing the influence of substituents on two reactions, their effect on one reaction may be compared with that on the equilibrium constant of a related process. As an illustration, the change of the specific rate of the reaction⁹⁰



resulting from different substituents R, may be compared with the influence of the same substituent on the equilibrium constant of the system,



i.e., on the dissociation constant of the acid $\text{R} \cdot \text{CO} \cdot \text{OH}$. The variation of the equilibrium constant K with the parameter x may be represented by an equation analogous to (132); thus,

$$\ln K_i^B = \text{const.} - \frac{g_B}{RT} d\chi_i^B, \quad (135)$$

where g_B is now equal to $\partial(\Delta F_i)/\partial T$ for the given equilibrium, ΔF_i being the standard free-energy change for the complete reaction concerned in the equilibrium, *i.e.*, ionization of the acid. Mak-

⁹⁰ L. P. Hammett and H. L. Pfluger, *J. Am. Chem. Soc.*, **55**, 4079 (1933).

ing the same assumptions as before, *viz.*, that dx_i^A/dx_i^B is a constant for any substituent i , then Eqs. (131) and (135) give

$$\ln k_i^A = C \frac{g_B}{g_A^\ddagger} \ln K_i^B + \text{const.} \quad (136)$$

Further, if g_B/g_A^\ddagger is a constant, *i.e.*, if the change in the activation free energy in going from one substituent to another is a definite fraction of the corresponding change in total free energy for an analogous equilibrium reaction, then, as before,

$$\log k_i^A = x \log K_i^B + \text{const.} \quad (137)$$

It is possible, in an exactly analogous manner, to relate the influence of a series of substituents on the equilibrium constants of two groups of reactions; in this way, the equation

$$\log K_i^A = x \log K_i^B + \text{const.} \quad (138)$$

is obtained.

Experimental confirmation of Eqs. (134), (137) and (138) can be found in a variety of published data.⁹¹ The empirical equations proposed by H. S. Taylor⁹² and by J. N. Brønsted and K. J. Pedersen⁹³ to relate the specific rate constant k_i of a reaction catalyzed by an acid, or base, to the dissociation constant K_i of the acid, or base, *viz.*,

$$k_i = GK_i^x, \quad (139)$$

where G and x are constants for a series of acidic, or basic, catalysts for a given reaction, are clearly identical with (137).

Entropy Relationship.—The question of the connection between specific reaction rate and equilibrium constant may be considered from a somewhat different point of view which leads to results of interest. It was shown in Chap. III that in a series of analogous reactions the change in activation energy, *e.g.*, in passing from one substituent to another, may be a definite fraction of the change in the heat of reaction. This was a consequence of the dissociation curve I in Fig. 46, (page 145) remaining the

⁹¹ For reviews, see L. P. Hammett, *Chem. Rev.*, **17**, 125 (1935); *Trans. Faraday Soc.*, **34**, 156 (1938); "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., 1940.

⁹² H. S. Taylor, *Z. Elektrochem.*, **20**, 201 (1914).

⁹³ J. N. Brønsted and K. J. Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

same, while the repulsion curve II moved vertically without change of shape. A similar phenomenon occurs when substituents leave curve II un-

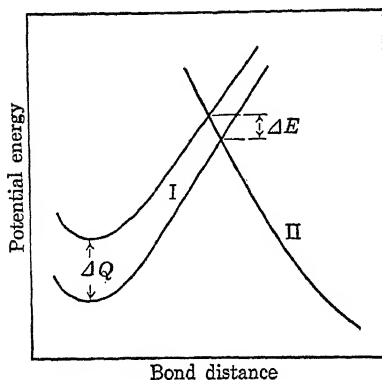


FIG. 112.—Potential-energy curves for reaction in which a substituent alters I but leaves II unchanged.

changed but merely alter the position of I, as shown in Fig. 112; this condition would arise when the substituted group affects the strength, or ionic character, of the bond broken in the rate-determining step of the reaction. It is readily seen that here, also, the change ΔE in energy of activation for a series of analogous reactions would be a definite

fraction of the change ΔQ in the heat of reaction.

Consider two reactions in the series, the rate constants being k_1 and k_2 ; then, by the theory of absolute reaction rates,

$$\frac{k_1}{k_2} = e^{(\Delta S_1^\ddagger - \Delta S_2^\ddagger)/R} e^{-(\Delta H_1^\ddagger - \Delta H_2^\ddagger)/RT}. \quad (140)$$

$$\ln \frac{k_1}{k_2} = \frac{\Delta S_1^\ddagger - \Delta S_2^\ddagger}{R} - \frac{\Delta H_1^\ddagger - \Delta H_2^\ddagger}{RT} \quad (141)$$

it being assumed that the transmission coefficient is the same in both cases. For any related equilibrium process, the mass action constants K_1 and K_2 are connected by an analogous equation

$$\ln \frac{K_1}{K_2} = \frac{\Delta S_1 - \Delta S_2}{R} - \frac{\Delta H_1 - \Delta H_2}{RT} \quad (142)$$

where ΔS and ΔH are now the standard free-energy and heat-content changes, respectively, for a complete reaction. According to Eq. (139),

$$\ln \frac{k_1}{k_2} = x \ln \frac{K_1}{K_2}, \quad (143)$$

and hence, from Eqs. (141) and (142),

$$\frac{\Delta S_1^\ddagger - \Delta S_2^\ddagger}{R} - \frac{\Delta H_1^\ddagger - \Delta H_2^\ddagger}{RT} = x \frac{\Delta S_1 - \Delta S_2}{R} - x \frac{\Delta H_1 - \Delta H_2}{RT} \quad (144)$$

If the change in substituent from 1 to 2 produces the same change in the heat of reaction of the equilibrium process as it does for the reaction whose rate is being measured, then $\Delta H_1 - \Delta H_2$ may be regarded as equal to the change in the heat of the latter reaction. As stated above, the change in the heat of activation, *i.e.*, $\Delta H_1^\ddagger - \Delta H_2^\ddagger$, should be a definite fraction of this quantity;⁹⁴ and if the fraction (x) is supposed to be the same x as appears in Eqs. (139) and (143), *i.e.*,

$$\Delta H_1^\ddagger - \Delta H_2^\ddagger = x(\Delta H_1 - \Delta H_2), \quad (145)$$

then Eq. (144) reduces to

$$\Delta S_1^\ddagger - \Delta S_2^\ddagger = x(\Delta S_1 - \Delta S_2). \quad (146)$$

The change in entropy of activation for a series of reactions should thus be a definite fraction of the corresponding change in the standard entropy of a related equilibrium process. Equation (146) has been confirmed by the results recorded for the iodination of acetone in the presence of a number of acids as catalyst. In Table LIX the suffix 1 refers in each case to the hydrogen ion (H_3O^+) as catalyst, the acid given in the first column representing the other, designated by the suffix 2; the ΔS values are the entropies of dissociation of the respective acids.⁹⁵

TABLE LIX.—RELATIONSHIP BETWEEN CHANGE IN ENTROPY OF ACTIVATION AND STANDARD ENTROPY OF COMPLETE REACTION

Catalyst	ΔS^\ddagger	ΔS	$\Delta S_1^\ddagger - \Delta S_2^\ddagger$	$\Delta S_1 - \Delta S_2$	x
H_3O^+	10.4	0
$\text{CH}_3\cdot\text{COOH}$	24.2	30.1	13.8	30.1	.46
$\text{C}_2\text{H}_5\cdot\text{COOH}$	26.7	30.9	16.3	30.9	.53
$\text{CH}_2\text{Cl}\cdot\text{COOH}$	21.2	25.1	10.8	25.1	.43
$\text{CHCl}_2\cdot\text{COOH}$	16.9	(13.0)	6.5	(13.0)	(.50)

The results are in agreement, at least approximately, with the requirements of Eq. (146); the entropy of ionization of dichloroacetic acid, given in parentheses, is estimated on the basis of an assumed mean value of x equal to 0.5.

⁹⁴ See, however, R. P. Bell and E. C. Baughan, *Proc. Roy. Soc.*, **158**, A, 464 (1937).

⁹⁵ Wynne-Jones and Eyring, Ref. 1.

Influence of Pressure on Reaction Velocity.⁹⁶—An important variable parameter, the influence of which on reaction rates may be considered by the aid of a suitable form of Eq. (130), is pressure. The free energy of activation ΔF^\ddagger may be written as equal to $F^\ddagger - F_i$, where these two quantities are the actual free energies in activated and initial states, respectively. Substitution for ΔF^\ddagger in Eq. (128) and differentiation with respect to pressure then give

$$\frac{d \ln k}{dp} = \frac{1}{RT} \left(\frac{\partial F_i}{\partial p} - \frac{\partial F^\ddagger}{\partial p} \right)_T \quad (147)$$

at constant temperature. It is known from thermodynamics that $\partial F/\partial p$ is equal to the molar volume, so that Eq. (147) can be written

$$\frac{d \ln k}{dp} = \frac{V_i - V^\ddagger}{RT} = \frac{-\Delta V^\ddagger}{RT} \quad (148)$$

For a bimolecular reaction the activated complex may be expected to have a smaller volume than the sum of the values for the

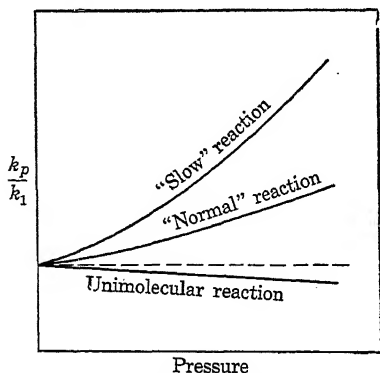


FIG. 113.—Variation with pressure of the ratio of the specific reaction (k_p) at pressure p to that (k_1) at 1 atm. pressure. (Perrin.)

reacting molecules, since they become associated to some extent, i.e., $V_i > V^\ddagger$, and so increase of pressure should increase the reaction rate. Measurements on a variety of bimolecular processes confirm this view:⁹⁷ if the reaction is a "normal" one (cf. page 6), i.e., if it is one having a small positive value of ΔS^\ddagger , e.g., the reaction between sodium ethoxide and ethyl iodide or the hydrolysis of sodium monochloracetate by sodium hydroxide, then

the increase of velocity with increasing pressure is relatively small (Fig. 113). For the so-called "slow reactions" having large negative values of ΔS^\ddagger , e.g., the formation of quaternary

⁹⁶ Evans and Polanyi, Ref. 89; Stearn and Eyring, Ref. 1.

⁹⁷ For summary, see M. W. Perrin, *Trans. Faraday Soc.*, **34**, 144 (1938).

ammonium salts or the esterification of ethyl alcohol by acetic anhydride, the effect of pressure is much more marked. When the activated complex has a much lower entropy than the reactant, as is the case with slow reactions, the former will presumably have a much more rigid structure than would be the case in a normal reaction. It may be argued, therefore, that the quantity $V_i - V^\ddagger$ will be greater for a slow than for a normal reaction, and so the increase in reaction rate with increasing pressure should be greater in the former than in the latter case.

If these views concerning the relationship between entropy of activation and the influence of pressure are extended to unimolecular reactions, it is apparent that, since the latter are generally accompanied by an increase of entropy, increase of pressure either should have little effect or might possibly decrease the reaction rate. Observations on the decomposition of phenylbenzylmethyl allyl ammonium chloride show that there is a 1.5-fold decrease in velocity when the pressure is increased to 3,000 atm. It is of interest to note that the rate of the reverse (bimolecular) process is accelerated 5 times by the same increase of pressure, while the factor calculated from the effect of pressure on the direct (unimolecular) reaction and on the equilibrium constant is 6.5.

It has been seen (page 419) that there is reason for believing that in reactions of the Menschutkin type the activated complex resembles the quaternary ammonium salt. As an approximation, therefore, V^\ddagger for this type of reaction may be taken as being the same as that of the product, so that $V_i - V^\ddagger$ is roughly equal to the decrease in volume accompanying the formation of the quaternary ammonium salt. For the reaction between pyridine, on the one hand, and ethyl and isopropyl iodide, on the other hand, the decrease in volume is 54.3 and 55.1 cc., respectively, per mole of product. If these figures are put equal to $V_i - V^\ddagger$, then $d \ln k/dp$ is found to be 2.22×10^{-3} and 2.25×10^{-3} per atmosphere, respectively; the experimental values are 0.69×10^{-3} and 0.75×10^{-3} .

Another approach to the problem of the influence of pressure on reaction rates is the following.⁹⁸ If the cross section of the reactants may be regarded as remaining virtually constant on

⁹⁸ A. E. Stearn and H. Eyring, unpublished.

activation, the change in volume ΔV^\ddagger is then essentially proportional to the change in over-all length. Consider, for example, the bimolecular reaction between a tertiary amine $R'R''R'''.N$ and an alkyl iodide $R.I$; the relative positions of the molecules at their closest approach, but before the activated complex is formed, may be represented as in Fig. 114. The dotted curves, indicating the minimum distance to which two nonbonded atoms can approach, are supposed to be 0.5 \AA. in each case from the outside of the atoms shown by the full circles. When the activated state is formed, the N atom and the R group come into contact, so that there is a decrease of 1 \AA. in the over-all length;

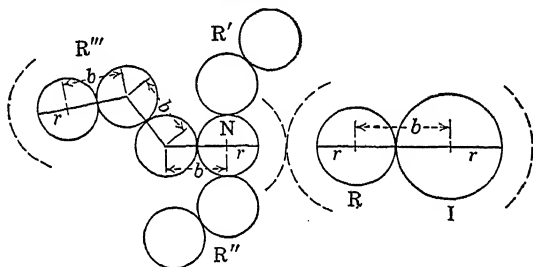


FIG. 114.—Closest approach of a tertiary amine $R'R''R'''.N$ to an alkyl iodide $R.I$ prior to the formation of the activated complex.

it follows, therefore, in view of the postulate concerning the constancy of the cross section, that

$$\Delta V^\ddagger = - \frac{\Sigma V}{\Sigma l}, \quad (149)$$

where ΣV is the sum of the molar volumes of the two reactants and Σl is defined by

$$\Sigma l = \Sigma b + \Sigma r + 2. \quad (150)$$

In this equation, Σb is the sum of the bond lengths, in angstrom units, from the ends of the reacting molecules farthest from the reacting group, or atom, to that group, or atom, and Σr is the sum of the covalent, or ionic, radii of the end atoms and of the reacting atoms, or ions (*cf.* Fig. 114); the additional 2 \AA. is accounted for by the envelopes, each 0.5 \AA. distant from its corresponding atom, as shown by the dotted curves. Combination of Eqs. (149) and (150) gives

$$\Delta V^\ddagger = - \frac{\Sigma V}{\Sigma b + \Sigma r + 2}. \quad (151)$$

In the case of unimolecular reactions the activated state may be regarded as being formed when the bond which is broken in the reaction is extended by 10 per cent of its original length (*cf.* page 459), so that, by use of the assumption of constant cross section, it follows that

$$\Delta V^\ddagger = \frac{0.1b^\ddagger}{\Sigma l} V, \quad (152)$$

where b^\ddagger is the length of the bond which is broken, V is the molar volume of the reactant, and Σl is the effective length of the molecule defined by

$$\Sigma l = \Sigma b + r_1 + r_2 + 1; \quad (153)$$

Σb is the sum of the bond lengths in the chain containing the activated bond, r_1 and r_2 are the covalent radii of the two terminal atoms, and 1 Å. is added for the envelopes, each 0.5 Å. in thickness, surrounding them.

The values of ΔV^\ddagger calculated by means of Eqs. (151) and (152) are recorded in Table LX; the corresponding figures for ΔV^\ddagger

TABLE LX.—INCREASE OF VOLUME ON ACTIVATION

Reaction	Pressure range, atm.	ΔV^\ddagger , cc.	
		Calc.	Obs.
Decomposition of phenylbenzylmethylallyl ammonium bromide.....	1 to 3,000	3.5*	3.4
Pyridine and methyl iodide.....	1 to 3,000	-15.8	-16.3
Pyridine and cetyl bromide.....	1 to 1,000	-12.3	-12.5
Acetic anhydride and ethyl alcohol.....	1 to 1,000	-13.3	-14.0
Ethoxyl ions and ethyl iodide.....	1 to 3,000	-11	-4
Alkaline hydrolysis of chloracetate ions.....	1 to 3,000	-8	-6
Alkaline saponification of:			
Ethyl acetate.....	250 to 500	-11	-5.5
Ethyl <i>o</i> -methyl cinnamate.....	1 to 500	-12.3	-13
Ethyl benzoate.....	1 to 1,500	-10.7	-13.6
Ethyl <i>o</i> -methoxybenzoate.....	1 to 1,500	-13.7	-13

* On the assumption that the N—Me bond is broken; for any other N—R bond the value would have been 2.7 cc.

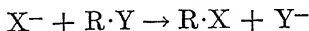
observed were obtained by means of Eq. (148) from measurements of the specific reaction rates at various pressures.⁹⁹

⁹⁹ Data from E. Cohen and H. F. G. Kaiser, *Z. physik. Chem.*, **89**, 338 (1914); A. L. T. Moesveld, *ibid.*, **105**, 455 (1923); A. L. T. Moesveld and

The agreement between observed and calculated values is satisfactory on the whole, and the rules given above may be regarded as a first step in the direction of the calculation of the influence of pressure on reaction rates in solution.

CALCULATION OF ACTIVATION ENERGIES¹⁰⁰

Halogen Exchange Reactions.—If, as has been suggested, for halogen exchange reactions of the general type



occurring in solution there is little or no resonance energy in the activated state, it should be possible to calculate the activation energies by the method described on page 142. The energy

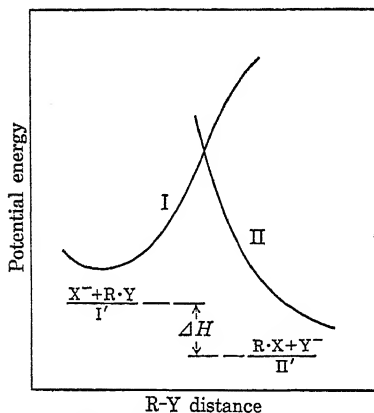


FIG. 115.—Potential-energy curves for reaction $X^- + R \cdot Y \rightarrow R \cdot X + Y^-$.

of the bond $R-Y$, which determines the shape of the dissociation curve I in Fig. 115, is obtained from the Morse curve for the $C-Y$ bond;* similarly, the displacement of the repulsion curve II above II' is given by the Morse curve for the $C-X$ bond. The extent to which I is raised above I' is determined partly by the energy of interaction E_m of the ion X and the homopolar molecule $R \cdot Y$, and partly by the energy E_s required to separate the ion X^- from its surrounding solvent

molecules. The value of E_m for X^- and $R \cdot Y$ is given by

$$E_m = \gamma_{X,R} + \delta_{X,R} + \eta_X, \quad (154)$$

W. A. T. de Meester, *ibid.*, **138**, 169 (1928); R. O. Gibson, E. W. Fawcett and M. W. Perrin, *Proc. Roy. Soc.*, **150**, A, 223 (1935); E. G. Williams, M. W. Perrin and R. O. Gibson, *ibid.*, **154**, A, 684 (1936); E. W. Fawcett and R. O. Gibson, *J. Chem. Soc.*, 396 (1934).

¹⁰⁰ R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, **31**, 604, 1375 (1938); A. G. Evans and M. G. Evans, *ibid.*, **31**, 1400 (1938).

*The Morse curve for the $C-Y$ bond, obtained from spectroscopic data, gives the energy of dissociation into C and Y atoms, whereas it is probably the energy of dissociation into ions that is required for the reaction under consideration.

where

$$\gamma_{X,R} = \frac{\varepsilon \mu_{C-Y}}{(r_{C-Y} + \Delta)^2} \quad (155)$$

is the electrostatic interaction of the charge ε on the ion X^- and the dipole of the $C-Y$ bond whose moment is μ_{C-Y} ; the term r_{C-Y} is the distance between the central carbon atom and Y , and Δ is the distance between the carbon atom and the point of operation of the dipole in the bond, which may be taken as equal to the radius of the carbon atom, *viz.*, 0.77 Å. The energy of polarization of the carbon atom in the field of the ionic charge X^- is given by

$$\delta_{X,R} = -\frac{\alpha}{2} \cdot \frac{\varepsilon^2}{(r_{X-C})^4}, \quad (156)$$

α being the polarizability of the carbon atom, *i.e.*, 9.3×10^{-25} , and r_{X-C} is the distance between the ion X^- and the central carbon atom. Finally η_X gives the nonelectrostatic repulsion which is taken to be analogous to the repulsive forces in crystals; it is given by $b e^{-r/\rho}$, where b and ρ have the same significance as the corresponding terms in Eq. (56), Chap. III. The calculation of the interaction energy E_s between the ion and the surrounding solvent molecules is simplified by the approximation of considering only one molecule of solvent as being concerned, and an equation analogous to Eq. (154), *viz.*,

$$E_s = \gamma_s + \delta_s + \eta_s \quad (157)$$

is assumed to apply. All the information is now available, in principle, for fixing the shape and position of the curve I. The form of curve II is determined by the appropriate value of $E_m + E_s$, obtained in a manner similar to that already described, and its position above II' is given by the Morse curve, as already explained. The distance between I' and II' is equal to the heat of reaction, and for the halogen exchange reactions under discussion this may be taken to be very small or zero.

Utilizing this method, R. A. Ogg and M. Polanyi¹⁰¹ calculated the minimum value of the energy for the point at which the curves I and II intersect, and this was taken to be the activation energy of the corresponding exchange reaction. The results

¹⁰¹ Ogg and Polanyi, Ref. 100.

obtained are recorded in Table LXI under the heading of E (calc.), while under E (obs.) are given some mean experimental values; the latter depend to some extent on the nature of the group R, but its influence is not likely to be very great.

TABLE LXI.—CALCULATED AND OBSERVED ACTIVATION ENERGIES FOR HALOGEN EXCHANGE REACTIONS

Reaction	E (calc.), kcal.	E (obs.), kcal.
$F^- + R \cdot F$	39	..
$Cl^- + R \cdot Cl$	31	22
$Br^- + R \cdot Br$	28	19
$I^- + R \cdot I$	25	17
$I^- + R \cdot F$	31	23
$I^- + R \cdot Cl$	28	22
$I^- + R \cdot Br$	26	18

The order of the calculated activation energies is similar to that of the experimental values, but there is a constant difference of about 8 kcal. between them. This may be due, among other causes, to the neglect of the resonance energy in the activated state; if it were so, this would have to be 8 kcal. It was seen in Chap. V (page 256) that for racemization and inversion reactions in the gas phase, which are similar to those under consideration, an appreciable amount of energy is required to force the three valences of the carbon into one plane in the activated complex. An analogous energy contribution will presumably be required in the halogen exchange reactions in solution, but in the foregoing treatment this has been taken to be negligibly small. If this energy were included, the discrepancy between observed and calculated activation energies would be even larger than in Table LXI.

CHAPTER IX

VISCOSITY AND DIFFUSION

FREE VOLUME OF A LIQUID

Holes in Liquids.—Both diffusion and viscosity can be treated by means of the theory of absolute reaction rates, but before proceeding with the development of the equations it is convenient to consider certain aspects related to the theory of the liquid state. Just as a gas is assumed to consist of molecules moving about in empty space, so a liquid may be regarded as made up of "holes" moving about in matter;¹ in fact, holes are to be considered as playing the same part in a liquid as molecules do in the gas phase.*

Suppose the N molecules forming a liquid are all bound to each other by "bonds," the total energy of which is $\frac{1}{2}NE$; to vaporize a single molecule would require $\frac{1}{2}E$, provided that the other molecules adjust their positions so as to leave no hole in the liquid. If a hole is to be left, however, the vaporization of a single molecule would require an energy E ; and so $E - \frac{1}{2}E$ *i.e.*, $\frac{1}{2}E$, is the energy necessary merely to make a hole of molecular size in the liquid, without vaporizing a molecule. It follows, therefore, that the same energy is required to make a hole in the liquid large enough for a molecule as to evaporate a molecule without leaving a hole. The latter quantity is equivalent to the energy of vaporization per molecule, *i.e.*, $\Delta E_{\text{vap.}}$ per mole, where $\Delta E_{\text{vap.}} = \Delta H_{\text{vap.}} - RT$; the quantity $\Delta H_{\text{vap.}}$ is the normal latent heat of vaporization, and RT is the correction for the external work done in vaporizing 1 mole of liquid, the vapor being assumed to behave as an ideal gas. The energy required to form a hole of molecular size in a liquid is thus equal to the energy of vaporization per molecule of the latter.

¹ H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936); J. O. Hirschfelder, D. P. Stevenson and H. Eyring, *ibid.*, **5**, 896 (1937).

* The holes in a liquid probably occupy a volume that is less than that occupied by a molecule.

Free Volume.—A liquid may be treated as if it were composed of individual molecules each moving in a volume v_f in an average potential field due to its neighbors, and the partition function of a molecule in the liquid may be represented by the expression²

$$F_l = \frac{(2\pi mkT)^{3/2}}{h^3} v_f b_l e^{-E_0/RT}, \quad (1)$$

where b_l is the combined vibrational and rotational contribution and E_0 is the difference in energy, per mole, between the molecules in the liquid and in the gas at 0°K. and hence may be identified, very approximately, with $\Delta E_{\text{vap.}}$, as defined above. The volume v_f is called the "free volume," and Eq. (1) may be taken as defining this quantity. According to thermodynamics the derivative of the Helmholtz free energy with respect to volume,

at constant temperature, gives the negative of the pressure, and hence it can be shown that for a liquid the external pressure p is given by

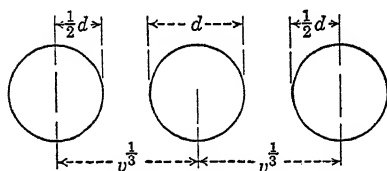


FIG. 116.—Determination of the free volume of a molecule from the volume inhabited and the diameter.

$$p = RT \left(\frac{\partial \ln F_l}{\partial v} \right)_T, \quad (2)$$

where v is equal to the total volume of the liquid divided by the number of molecules contained in it. It follows, therefore, from Eqs. (1) and (2) that

$$p = RT \left(\frac{\partial \ln v_f}{\partial v} \right)_T - \left(\frac{\partial \Delta E_{\text{vap.}}}{\partial v} \right)_T \quad (3)$$

It is now necessary to derive a relationship between the free volume v_f and the volume v inhabited by a molecule in the liquid. Consider, for simplicity, cubical packing in the liquid; one molecule may be regarded as oscillating about the origin, and the six nearest neighbors are supposed to be fixed in their mean positions along three axes. One of these axes is depicted in Fig. 116; each molecule is seen to be at a distance of $v^{1/3}$ from the origin. If d is the incompressible diameter of each molecule,

² H. Eyring and J. O. Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937); J. O. Hirschfelder, *J. Chem. Ed.*, **16**, 540 (1939).

$2v^{1/3} - 2d$ is the distance the central atom is free to move along each axis, and the free volume is $(2v^{1/3} - 2d)^3$, i.e.,

$$v_f = 8(v^{1/3} - d)^3. \quad (4)$$

It may be supposed that a similar equation will hold for other types of packing of the molecules in the liquid, so that, in general,

$$v_f = c^3(v^{1/3} - d)^3, \quad (5)$$

where c may not necessarily equal 2 and may vary with the temperature. Differentiation of Eq. (5) with respect to v gives

$$\left(\frac{\partial \ln v_f}{\partial v}\right)_T = \frac{c}{v^{2/3}v_f^{1/3}}, \quad (6)$$

and hence it follows from Eq. (3) that

$$\left[p + \left(\frac{\partial \Delta E_{\text{vap.}}}{\partial v}\right)_T\right] v^{2/3}v_f^{1/3} = cRT. \quad (7)$$

It is a reasonable approximation to replace $\partial(\Delta E_{\text{vap.}})/\partial v$ by $\Delta E_{\text{vap.}}/v$; and, further, the pressure p can generally be neglected in comparison with this quantity, so that Eq. (7) becomes

$$\Delta E_{\text{vap.}} \frac{v_f^{1/3}}{v^{1/3}} = cRT. \quad (8)$$

If v is replaced by V/N , where V is the molar volume of the liquid and N is the Avogadro number, then

$$v_f^{1/3} = \frac{cRTV^{1/3}}{N^{1/3}\Delta E_{\text{vap.}}}, \quad (9)$$

by means of which the free volume of the molecules in the liquid can be calculated.

Another method of deriving this quantity makes use of the difference in velocity of sound in liquid and gas.³ For most liquids the velocity of sound is greater by a factor of 5 to 10 than the average kinetic-theory velocity of the molecules; this difference can arise in the following manner. Suppose that there are three molecules A, B and C in a line, and suppose the wave front travels from the inner edge of the molecule A to the

³ J. F. Kincaid and H. Eyring, *J. Chem. Phys.*, **6**, 620 (1938).

adjacent edge of B by the velocity of sound (u_{gas}) applicable to an ideal gas; this is given by kinetic theory as

$$u_{\text{gas}} = \left(\frac{RT\gamma}{M} \right)^{\frac{1}{2}} \quad (10)$$

where γ is the ratio of the specific heats of the gas and M is the molecular weight. As A collides with B, however, the signal is transmitted almost instantaneously to the opposite edge of B;

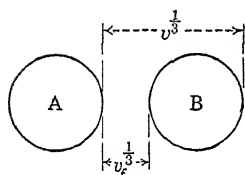


FIG. 117.—Determination of free volume of a molecule from velocity of sound.

thus, although the wave front moves apparently through the distance $v_f^{1/3}$, it effectively travels a distance $v^{1/3}$, as seen in Fig. 117. It follows, therefore, that

$$\frac{u_{\text{liq.}}}{u_{\text{gas}}} = \left(\frac{v}{v_f} \right)^{\frac{1}{3}}, \quad (11)$$

where $u_{\text{liq.}}$ is the velocity of sound in the liquid; hence, from Eqs. (10) and (11),

$$u_{\text{liq.}} = \left(\frac{v}{v_f} \right)^{\frac{1}{3}} \left(\frac{RT\gamma}{M} \right)^{\frac{1}{2}} \quad (12)$$

so that the free volume of a liquid can be calculated from the velocity of sound in it.

Both methods given above for calculating the free volume are to some extent approximate, but the one depending on measurements of the velocity of sound is probably the better of the two.

VISCOSITY

Flow as a Rate Process.⁴—Since the flow of a liquid is a rate process, in so far as it takes place with a definite velocity under given conditions, it seems reasonable to suppose that the theory of absolute reaction rates can be applied to the problem of viscosity. Consider two layers of molecules in a liquid, at a distance λ_1 apart, and suppose that one slides past the other

⁴ Eyring, Ref. 1; R. H. Ewell and H. Eyring, *ibid.*, **5**, 726 (1937); for review, see R. H. Ewell, *J. App. Phys.*, **9**, 252 (1938); cf. also J. Frenkel, *Z. Physik*, **35**, 652 (1926).

under the influence of an applied force; if f is the force per square centimeter tending to displace one layer with respect to the other and Δu is the difference in the velocity of the two layers, then by definition

$$\eta \equiv \frac{f\lambda_1}{\Delta u}, \quad (13)$$

where η is the coefficient of viscosity. For the purpose of the present treatment the motion of one layer with respect to another is assumed to involve the passage of a molecule from one equilibrium position to another such position in the same layer. In order that this passage shall occur, it is necessary that a suitable hole or site shall be available, and the production of such a site requires the expenditure of energy since work must be done in pushing back other molecules. The jump of the moving molecule from one equilibrium position to the next may thus be regarded as equivalent to the passage of the system over a potential-energy barrier. Let λ be the distance between two equilibrium positions in the direction of motion, the distance between neighboring molecules in the same direction being λ_3 ; the latter is not necessarily equal to λ , but it may be so approximately. Finally, the mean distance between two adjacent molecules in the moving layer in the direction at right angles to the direction of motion is λ_2 (Fig. 118). It is reasonable to suppose that the potential-energy barrier is a symmetrical one, and so the distance between the initial equilibrium position and the activated state, *i.e.*, the top of the barrier, is $\frac{1}{2}\lambda$ (Fig. 119), *i.e.*, half the distance between the initial and final positions of the molecule. The applied force acting on a single molecule in the direction of motion is $f\lambda_2\lambda_3$, since $\lambda_2\lambda_3$ is the effective area per molecule; hence, the energy that the moving molecule acquires when it has reached the top of the potential-energy barrier is $f\lambda_2\lambda_3 \times \frac{1}{2}\lambda$, *i.e.*, $\frac{1}{2}f\lambda_2\lambda_3\lambda$. The effect of the force

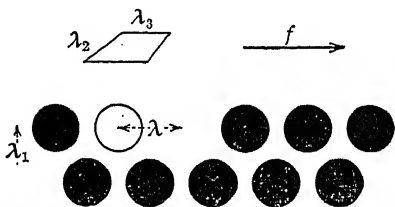


FIG. 118.—Distances between molecules in a liquid; λ is the distance between two equilibrium positions for viscous flow.

causing the flow of liquid is thus to reduce the height of the energy barrier in the forward direction by an amount $\frac{1}{2}f\lambda_2\lambda_3\lambda$, and the height in the opposite direction will be raised by the same amount (see Fig. 119).

If ϵ_0 is the energy of activation at 0°K. , *i.e.*, the height of the barrier, when no force is acting on the liquid, then, according to the theory developed in Chap. IV, the number of times a

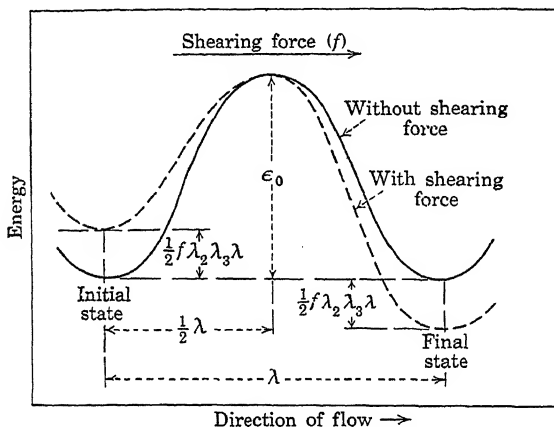


FIG. 119.—Potential-energy barrier for viscous flow, with and without shearing force.

molecule passes over the barrier, and hence moves in any direction, per second is given by

$$k = \frac{kT}{h} \cdot \frac{F_{\ddagger}}{F} e^{-\epsilon_0/kT}, \quad (14)$$

it being assumed that the transmission coefficient κ (page 190) is unity and the tunneling factor (page 191) being neglected. In this equation, F_{\ddagger} and F are the partition functions, for unit volume, of the molecule in the activated and initial states, respectively; the value of the former does not include the contribution of the degree of translational freedom normal to the barrier (page 189). Since the height of the barrier is altered by $\frac{1}{2}f\lambda_2\lambda_3\lambda$ when the force causing the liquid to flow is applied, the specific rate of flow in the forward direction, *i.e.*, in the direction of the force is

$$k_f = \frac{kT}{h} \cdot \frac{F_{\ddagger}}{F} e^{-(\epsilon_0 - \frac{1}{2}f\lambda_2\lambda_3\lambda)/kT} \quad (15)$$

$$= k e^{\frac{1}{2}f\lambda_2\lambda_3\lambda/kT}. \quad (16)$$

and the specific rate in the backward direction will be

$$k_b = k e^{-\frac{1}{2}f\lambda_2\lambda_3\lambda/kT}. \quad (17)$$

Each time a molecule passes over the potential barrier, it moves through a distance λ ; and since k_f and k_b give the numbers of times a molecule traverses the barrier per second, in the forward and backward directions, respectively, it follows that the distance moved by the molecule per second, and hence also the rate of motion of the layer, is given by $k_f\lambda$ in one direction and $k_b\lambda$ in the other. The net rate of flow in the forward direction as a result of the application of the force f , which by definition is Δu , is thus equal to $(k_f - k_b)\lambda$; and consequently, by Eqs. (16) and (17),

$$\Delta u = \lambda k (e^{\frac{1}{2}f\lambda_2\lambda_3\lambda/kT} - e^{-\frac{1}{2}f\lambda_2\lambda_3\lambda/kT}) \quad (18)$$

$$= 2\lambda k \sinh \frac{f\lambda_2\lambda_3\lambda}{2kT}. \quad (19)$$

If the relationship from Eq. (13) for the coefficient of viscosity is introduced, it follows that

$$\eta = \frac{\lambda_1 f}{2\lambda k \sinh (f\lambda_2\lambda_3\lambda/2kT)}. \quad (20)$$

For ordinary viscous flow, f is relatively small, of the order of 1 dyne per sq. cm.; and since λ_2 , λ_3 and λ are all of about molecular dimensions, *i.e.*, 10^{-8} cm., it follows that $2kT \gg f\lambda_2\lambda_3\lambda$. It is thus possible, in expanding the exponentials included in Eq. (20), to neglect all terms beyond the first; the result is

$$\eta = \frac{\lambda_1 kT}{\lambda_2\lambda_3\lambda^2 k}. \quad (21)$$

If the expression for the frequency k , as given by Eq. (14), is now inserted in (21), this becomes

$$\eta = \frac{\lambda_1 h}{\lambda_2\lambda_3\lambda^2} \cdot \frac{F}{F_{\ddagger}} e^{\epsilon_0/kT}. \quad (22)$$

Although λ is not necessarily equal to λ_1 , the two quantities are of the same order of magnitude; and if, as a first approximation, they are taken to be identical, Eq. (22) can be written as

$$\eta = \frac{h}{\lambda_2\lambda_3\lambda_1} \cdot \frac{F}{F_{\ddagger}} e^{\epsilon_0/kT}. \quad (23)$$

The product $\lambda_2\lambda_3\lambda_1$ is approximately the volume inhabited by a single molecule in the liquid state, and hence it may be put equal to V/N , where V is the molar volume and N is the Avogadro number; substitution in Eq. (23) then gives

$$\eta = \frac{hN}{V} \cdot \frac{F}{F^\ddagger} e^{\epsilon_0/kT}. \quad (24)$$

This equation may be written in another form by utilizing the identity (see page 188)

$$K^\ddagger = \frac{F^\ddagger}{F} e^{-\epsilon_0/kT}, \quad (25)$$

and the thermodynamic relationship

$$K^\ddagger = e^{-\Delta F^\ddagger/RT}, \quad (26)$$

where ΔF^\ddagger is the standard free energy of activation per mole. It follows from Eq. (24), therefore, that

$$\eta = \frac{hN}{V} e^{\Delta F^\ddagger/RT}. \quad (27)$$

Further, since ΔF^\ddagger may be replaced by $\Delta H^\ddagger - T \Delta S^\ddagger$, it is seen that

$$\eta = \left(\frac{hN}{V} e^{-\Delta S^\ddagger/R} \right) e^{\Delta H^\ddagger/RT}. \quad (28)$$

Since the molar volume of a liquid does not vary greatly with the temperature, and ΔS^\ddagger being taken as constant, Eq. (28) takes the form

$$\eta = B e^{E_{vis}/RT}. \quad (29)$$

A relationship of this kind was suggested empirically by S. Arrhenius⁵ and by J. de Guzmán⁶ and derived theoretically in a manner different from that given above by E. N. da C. Andrade;⁷ there is little doubt that it is in excellent agreement with experiment for many liquids.

⁵ Cf. S. Arrhenius, *Meddel. Vetenskapsakad. Nobelinst.*, **3**, [20] (1916).

⁶ J. de Guzmán, *Anales soc. españ. fis. quim.*, **11**, 353 (1913). See also Ewell, Ref. 4, for references to similar equations.

⁷ E. N. da C. Andrade, *Phil. Mag.*, **17**, 497, 698 (1934).

The partition function for a molecule of liquid may be written [cf. Eq. (1)]

$$F = \frac{(2\pi mkT)^{3/2}}{h^3} v_f b_l e^{-E_0/RT}, \quad (30)$$

where the first term on the right-hand side is the translational contribution of a single molecule moving in its free volume v_f ; b_l is the combined rotational and vibrational partition function. The chief difference between a molecule in the initial state and one in the activated state for flow is that the latter has one degree of translational freedom less than the former (cf. page 189), and if the product of $F_{\text{rot.}}$ and $F_{\text{vib.}}$ is almost the same in the two states, as it generally will be since the corresponding degrees of freedom are not affected, it follows that*

$$\frac{F}{F_{\ddagger}} = \frac{(2\pi mkT)^{1/2}}{h} v_f^{1/2}. \quad (31)$$

Substituting this term in Eq. (24) gives

$$\eta = \frac{N}{V} (2\pi mkT)^{1/2} v_f^{1/2} e^{E_0/kT}. \quad (32)$$

According to Eq. (9) the free volume may be represented, at least approximately, by the expression

$$v_f^{1/2} = \frac{cRTV^{1/2}}{N^{1/2}\Delta E_{\text{vap.}}}, \quad (33)$$

where $\Delta E_{\text{vap.}}$ is the molar energy of vaporization, c is the packing number as defined on page 479 and V and N have the same significance as above. It follows, therefore, that Eq. (32) may be written

$$\eta = \left(\frac{N}{V}\right)^{3/2} \frac{cRT}{\Delta E_{\text{vap.}}} (2\pi mkT)^{1/2} e^{E_0/kT}. \quad (34)$$

Upon taking c as equal to 2, *i.e.*, for cubic packing, inserting the

* Strictly speaking this equation should involve μ , the reduced mass of the reacting system in the direction of motion, instead of m ; the equation holds, however, if only one molecule is supposed to be moving, as appears to be generally the case.

known values for N and k and expressing R in calories, so that $\Delta E_{\text{vap.}}$ is also in calories, Eq. (34) becomes

$$\eta = 1.09 \times 10^{-3} \times \frac{M^{1/2} T^{3/2}}{V^{2/3} \Delta E_{\text{vap.}}} e^{E/RT}, \quad (35)$$

where M is the molecular weight of the substance under consideration and E is the activation energy per mole for viscous flow.* The molar heats of vaporization of many liquids are about 5,000 cal.; if the molecular weight of the substance is 121 and its molar volume is 125 cc., at ordinary temperatures, then

$$\eta \approx 0.4 \times 10^{-3} e^{E/RT}. \quad (36)$$

It is of interest to record that according to E. N. da C. Andrade⁹ the viscosity of many liquids can be expressed by means of an equation of the form $\eta = aV^{1/3} e^{b/T}$; a is found by experiment to be approximately 0.4×10^{-3} for many substances, and hence if the molar volume V is taken as 125 the result is approximately one-fifth of that given by Eq. (36).

It should be noted incidentally that in Eq. (35) the term $T^{3/2}$ appears in the nonexponential part of the velocity equation; it follows, therefore, that the factor B in Eq. (29) cannot be independent of temperature.

Viscosity (or Fluidity) and Holes in Liquids.⁹—If a hole is necessary for a liquid to flow, as was postulated on page 481, it is reasonable to assume that the fluidity of a liquid will be proportional to the number of holes. In the interpretation of the Caillietet-Mathias law of the rectilinear diameter, it has been suggested that the expansion of a liquid is largely due to the introduction of holes into the system.¹⁰ It follows, therefore, if the view that fluidity is related to the number of holes is correct, that the fluidity of a liquid at constant volume should remain constant irrespective of changes of temperature and pressure. It is of interest to record that the data on viscosities at high pressures show that for nonassociated liquids the temper-

* A bimolecular flow mechanism, which is, however, improbable, would give a factor of $1.09 \times 10^{-3}/\sqrt{2} = 7.71 \times 10^{-4}$, since μ which then appears instead of m in Eq. (34) is $m/2$.

⁸ Andrade, Ref. 7.

⁹ R. E. Powell, W. E. Roseveare and H. Eyring, unpublished.

¹⁰ Eyring, Ref. 1.

ature coefficient of fluidity at constant volume is insignificant in comparison with that at constant pressure.¹¹ Further support for the relationship between the fluidity and the number of holes can be obtained in other ways. The essential difference between a solid and a liquid may be regarded as the introduction of holes (*cf.* page 477), so that if V is the molar volume of a liquid and V_s is that of the unexpanded solid, the difference, *i.e.*, $V - V_s$, is proportional to the number of holes in the liquid and hence to its fluidity. Since the fluidity is the reciprocal of the coefficient of viscosity, it follows that

$$\eta = \frac{c}{V - V_s}, \quad (37)$$

where c is a constant. This result is identical in form with the equation proposed by A. J. Batschinski¹² and found by him to hold for a large number of nonassociated liquids.

The entropy of fusion of monatomic solids, and also of some others of a complex nature which rotate equally in liquid and solid states, is known to be approximately 2 E.U.¹³ This result may be accounted for by supposing that a liquid is a random mixture of molecules and unoccupied equilibrium positions or holes, there being a constant ratio between the number of molecules and the number of holes at the melting point. If N molecules, where N is the Avogadro number, are mixed with n_h holes, the increase of entropy, which should be equivalent to the entropy of fusion, is given by

$$\Delta S = -Nk \ln \left(\frac{N}{N + n_h} \right) - n_h k \ln \left(\frac{n_h}{N + n_h} \right); \quad (38)$$

and if this is put equal to 2 cal. per degree per mole, it is found that n_h is equal to $0.54N$. It follows, therefore, that for simple substances having an entropy of fusion of 2 E.U., the process of fusion is accompanied by the introduction of a definite number of holes; if the fluidity is a function of the number of holes alone, the fluidity or viscosity of such substances should all be the

¹¹ Data from P. M. Bridgman, "The Physics of High Pressure," The Macmillan Company, 1931.

¹² A. J. Batschinski, *Z. physik. Chem.*, **84**, 643 (1913).

¹³ E. Kordes, *Z. anorg. Chem.*, **160**, 67 (1927); see also J. O. Hirschfelder, D. P. Stevenson and H. Eyring, *J. Chem. Phys.*, **5**, 896 (1937).

same at their respective melting points. The viscosities of mercury, cadmium, lead, bismuth, carbon disulfide and carbon tetrachloride and of some of the lower paraffins are approximately 0.02 poise at their melting points.

In view of the relationship between fluidity and the number of holes, an alternative treatment of viscosity by the theory of absolute reaction rates is possible.¹⁴ The total activation energy for viscous flow may be regarded as consisting of two parts: (1) the energy required to form the hole, (2) that required for the molecule to move into the hole. In view of the foregoing discussion, it is evident that for many substances the latter contribution to the activation energy is small, and this is shown more definitely by the following treatment. The number of equilibrium positions, or holes, available is obtained on dividing $v - v_s$, where these quantities refer to a single molecule, by v_h , the increase in volume per equilibrium position. The average velocity of the molecules parallel to the direction of flow (cf. page 186) is $(kT/2\pi m)^{1/2}$; the distance moved forward by the molecule in each jump is λ , and hence the specific rate of flow of molecules in a forward direction in the absence of a shearing force is

$$k_f = \frac{v - v_s}{v_h} \cdot \frac{1}{\lambda} \left(\frac{kT}{2\pi m} \right)^{1/2} e^{-\Delta\epsilon_f/kT}, \quad (39)$$

$$= k_1 e^{-\Delta\epsilon_f/kT}, \quad (40)$$

where $\Delta\epsilon_f$ is the activation energy required for a single molecule to flow into a hole that is already available. If a shearing force is applied, the specific rate in the forward direction is

$$k_f = k_1 e^{-(\Delta\epsilon_f - \frac{1}{2} f \lambda_2 \lambda_3 \lambda)/kT}, \quad (41)$$

and the specific rate in the backward direction is

$$k_b = k_1 e^{-(\Delta\epsilon_f + \frac{1}{2} f \lambda_2 \lambda_3 \lambda)/kT}. \quad (42)$$

Upon utilizing Eq. (13) in the reciprocal form $\phi = \Delta u / f \lambda_1$, where ϕ is the fluidity, and the definition of Δu on page 481, it follows that

$$\phi = \frac{\lambda k_1}{f \lambda_1} e^{-\Delta\epsilon_f/kT} 2 \sinh \frac{f \lambda_2 \lambda_3 \lambda}{2kT}. \quad (43)$$

¹⁴ Powell, Roseveare and Eyring, Ref. 9.

Making the same approximation as before that

$$2kT \gg f\lambda_2\lambda_3\lambda$$

and introducing the value of k_1 from Eq. (39), this equation reduces to

$$\phi = \frac{\lambda\lambda_2\lambda_3}{\lambda_1} \cdot \frac{v - v_s}{v_h} (2\pi mkT)^{-1/2} e^{-\Delta E_f/kT}. \quad (44)$$

If the ratio of the λ terms is taken as being independent of the temperature and if ϕ_1 and ϕ_2 are the fluidities at constant volume at the temperatures T_1 and T_2 , respectively, then

$$-\Delta E_f \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = R \ln \frac{\phi_1}{\phi_2} + \frac{1}{2} R \ln \frac{T_1}{T_2}, \quad (45)$$

where ΔE_f is the activation energy per mole for molecules to move into the prepared holes. It is possible, therefore, to derive ΔE_f from viscosity data at constant volume at two temperatures; it has been found in this way that for a number of substances, *e.g.*, metals, hydrocarbons, phenyl halides, carbon disulfide and carbon tetrachloride, the value is of the order of 500 cal., which is about one-fifth to one-tenth of the total activation energy for flow. It follows, therefore, that most of the energy is required for the preparation of the holes into which the molecules move. Alcohols have ΔE_f values of 3 to 4 kcal., which is approximately the energy required to break a hydrogen bond. For hydroxylic compounds and associated substances generally, there is, therefore, an appreciable activation energy necessary for the movement of the molecule, apart from that required to make the hole for the molecule to flow into; the reason for this is considered more fully on page 505. For water, ΔE_f is negative, and this suggests a change in structure or coordination number with temperature at constant volume (*cf.* page 505).

It can be shown by the arguments on page 487 that, at the melting point of a substance for which the entropy of fusion is 2 E.U., the fraction $(v - v_s)/v_h$ is equal to 0.54; further, if the quantity $\lambda\lambda_2\lambda_3/\lambda_1$ is replaced by $(V/N)^{3/2}$, where V is the molar volume of the liquid at the melting point, Eq. (44) becomes

$$\phi_m = 0.54 \left(\frac{V}{N} \right) (2\pi mkT)^{-1/2} e^{-\Delta E_f/RT}. \quad (46)$$

If ΔE_f is taken as about 500 cal., as recorded above for substances whose activation energy for flow is required mainly to make a hole for the molecule to move into, then according to Eq. (46) the fluidity at the melting point (ϕ_m) should be of the order of 100; this is in agreement with the fact mentioned above that the viscosity is approximately 0.02 poise.

Comparison of Gas and Liquid Viscosities.¹⁵—In the suggested mechanism for viscosity, it is necessary that the molecule, after making a jump from one equilibrium position to the next, should remain at the latter point long enough to dissipate the energy it possessed while passing over the energy barrier. The molecule must, therefore stay at each potential-energy minimum until the Maxwell distribution of energy is restored. If this condition is not fulfilled, then it is probably more satisfactory to assume the mechanism to involve the transfer of momentum from one layer to the next by molecules passing back and forth between them; this mechanism is generally regarded as applicable to the flow of gases. If the actual activation energy $\epsilon_0 - \frac{1}{2}f\lambda_2\lambda_3\lambda$ in Eq. (15) is relatively large, *e.g.*, more than about $2kT$, then the molecule will undergo sufficient collisions between passages over successive barriers* for equilibrium statistics to apply, but for lower activation energies this condition will not hold. It has been suggested¹⁶ that the momentum-transfer theory applies to liquids as well as to gases, with the modification that in the former case the vibrational energy is transferred, instead of translational energy as for the latter. Excellent numerical agreement between the experimental results and expectations based on this theory were obtained for metals, but it is of interest to note that it is just for these substances that $\epsilon_0 - \frac{1}{2}f\lambda_2\lambda_3\lambda$, as estimated from the experimental results, is small, so that gaslike transfer of momentum is not unexpected.

In the extreme case, when ϵ_0 is zero, as for gases, and by writing $(2\pi mkT)^{1/2}\lambda/h$ for the ratio of the partition functions F/F_+ , *i.e.*,

¹⁵ Eyring, Ref. 1.

* The time between successive passages in the forward direction is

$$\frac{1}{k_f} = \frac{F}{F_+} \cdot \frac{h}{kT} e^{(\epsilon_0 - \frac{1}{2}f\lambda_2\lambda_3\lambda)/kT}.$$

¹⁶ Andrade, Ref. 7.

the free volume is supposed to be λ^3 , Eq. (23) takes the form

$$\eta \approx \frac{\lambda(2\pi mkT)^{1/2}}{\lambda_2\lambda_3\lambda_1}; \quad (47)$$

and if all the λ 's are taken to be equal, then

$$\eta \approx \frac{(2\pi mkT)^{1/2}}{\lambda^2}, \quad (48)$$

which is of the form

$$\eta = BT^{1/2}. \quad (49)$$

According to this equation the viscosity should increase in a manner approximately proportional to the square root of the temperature; this is the type of behavior actually observed with gases. The familiar equation for the viscosity of a gas is

$$\eta_{\text{gas}} = \frac{1}{3}n\bar{c}ml, \quad (50)$$

where n is the number of molecules per cubic centimeter, \bar{c} is their mean velocity, m is the mass of a molecule, and l is the mean free path. The mean velocity, according to kinetic theory, is given by

$$\bar{c} = \left(\frac{8kT}{\pi m} \right)^{1/2}, \quad (51)$$

and hence

$$\eta_{\text{gas}} = \frac{2nl}{3\pi} (2\pi mkT)^{1/2}. \quad (52)$$

This equation resembles (47) and is of the same general form as Eq. (49).

Free Energy of Activation for Flow and Energy of Vaporization. For a molecule to take part in flow a hole must be available; this hole is not necessarily the full size of a molecule but will be some fraction represented by the additional volume required by the activated state as compared with the initial state. The work required to make a hole of molecular size is equal to the energy of vaporization ΔE_{vap} . (see page 477), and so the free energy of activation may be expected to be some fraction of the energy of vaporization.

According to Eq. (27),

$$e^{\Delta F_{\text{vis.}}^{\ddagger}/RT} = \frac{V\eta}{hN}; \quad (53)$$

$$\therefore \Delta F_{\text{vis.}}^{\ddagger} = RT \ln \frac{V\eta}{hN}, \quad (54)$$

and hence it is a reasonably simple matter to determine the free energy of activation, provided that the viscosity and molar volume of a liquid are known at any temperature. A comparison

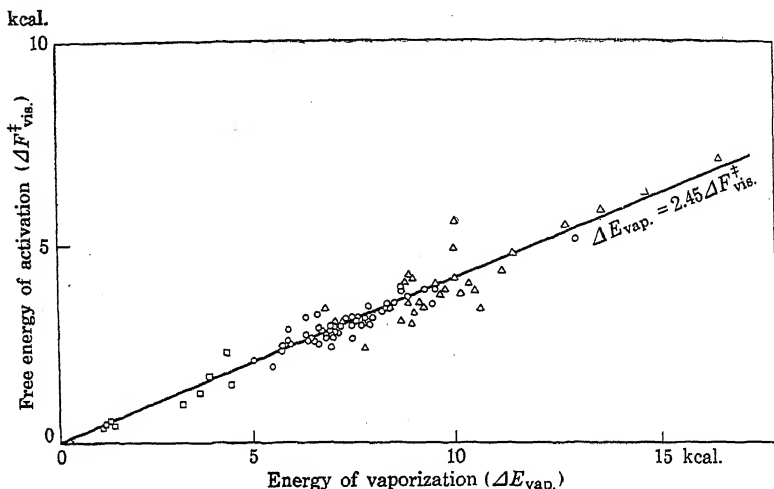


FIG. 120.—Relation between free energy of activation for viscous flow and energy of vaporization. (Roseveare, Powell and Eyring.)

of the values of $\Delta F_{\text{vis.}}^{\ddagger}$ obtained in this manner with the energies of vaporization, in Fig. 120,* has brought to light the important relationship

$$\frac{\Delta E_{\text{vap.}}}{\Delta F_{\text{vis.}}^{\ddagger}} = 2.45, \quad (55)$$

which has been found to hold for nearly 100 substances, excluding metals but including associated liquids. The free energy for the formation of a hole for a molecule to flow into is thus a constant fraction, somewhat more than one-third, of the energy

* In this figure, squares are used to represent substances that are gaseous at ordinary temperatures, triangles for alcohols and circles for other substances.

of vaporization of a molecule. It is a remarkable fact, the significance of which will be discussed later, that the same result is obtained for water and other associated liquids, even glycerol, as for nonpolar substances such as hydrocarbons.¹⁷

Theoretical Calculation of Viscosity.—The relationship between $\Delta E_{\text{vap.}}$ and $\Delta F_{\text{vis.}}$ [†] derived above may be used to calculate the viscosity of a liquid, provided that its molar volume and energy of vaporization are known, for combination of Eqs. (27) and (55) gives

$$\eta = \frac{hN}{V} e^{\Delta E_{\text{vap.}}/2.45RT} \quad \text{Eq. (56)} \quad \frac{hN}{V} \frac{\Delta E_{\text{vis.}}}{RT} \quad \text{(56)}$$

The use of Eq. (55) permits the derivation of the free energy of activation for viscous flow with an error of not more than 6 per cent, and hence the viscosity can be predicted within less than about 30 per cent by means of Eq. (56); this is a striking achievement of the theory of absolute reaction rates.

Energy of Activation for Flow and Energy of Vaporization.¹⁸—Since the energy of activation for viscous flow is related to the work required to form a hole in the liquid, the experimentally observed activation energy $E_{\text{vis.}}$ may be expected to be some fraction of $\Delta E_{\text{vap.}}$;* thus,

$$E_{\text{vis.}} = \frac{\Delta E_{\text{vap.}}}{n} \quad (57)$$

The same conclusion may be reached in a general manner from Eq. (55) by assuming a linear relationship between the heat and entropy of activation (*cf.* page 409). If the value of $E_{\text{vis.}}$ given by Eq. (57) is now inserted in (35) the result is

$$\eta = 1.09 \times 10^{-3} \times \frac{M^{1/2} T^{3/2}}{V^{2/3} \Delta E_{\text{vap.}}} e^{\Delta E_{\text{vap.}}/nRT} \quad (58)$$

In order to determine the factor n , which gives an indication of the size of the hole necessary for viscous flow, the viscosities

¹⁷ Powell, Roseveare and Eyring, *Ind. Eng. Chem.*, **33**, 430 (1941).

¹⁸ Ewell and Eyring, *Ref. 4*.

* It may be pointed out here that the activation energy for viscosity, *i.e.*, $\Delta E_{\text{vis.}}$, differs from the *free energy* of activation, $\Delta F_{\text{vis.}}$ [†], considered in the previous section, on account of the entropy change accompanying activation for viscous flow (see page 505).

were computed from Eq. (58), by use of integral and half-integral values of n from 2 to 5, and the resulting figures for $\log \eta$ plotted against $1/T$. For any value of n the plot was either a straight line or, in some cases, a curve slightly convex toward the $1/T$ axis; the value of n that gave a plot parallel to the straight line of the computed data for $\log \eta$ against $1/T$ was taken as the correct one. From an examination of the results for a number of substances, it is clear that for most nonassociated liquids, apart from metals, n lies between 3 and 4. It appears that for nonpolar molecules which have spherical or approximately spherical symmetry n is nearer 3; but for polar molecules and others, *e.g.*, long-chain hydrocarbons not having spherical symmetry, n is about 4.* It is doubtful, however, if a sharp distinction can be drawn, since the value of n increases with the temperature.¹⁹ The fact that for such a wide variety of non-associated substances the ratio of the heat of vaporization to the activation energy for viscous flow lies within relatively narrow limits is very striking; taken in conjunction with the discussion on page 477, this suggests that the energy required to make a hole for a molecule to flow into is approximately one-quarter of the energy of vaporization.

An alternative method of comparing $E_{\text{vis.}}$ and $\Delta E_{\text{vap.}}$ is to employ the value of $E_{\text{vis.}}$ derived from the experimental variation of viscosity with temperature; it follows from Eq. (29), for example, that; provided the entropy of activation for flow does not change with temperature,

$$E_{\text{vis.}} = R \frac{d \ln \eta}{d(1/T)}, \quad (59)$$

so that $E_{\text{vis.}}$ can be determined from the plot of $\log \eta$ against $1/T$, *i.e.*, in a manner similar to that employed for obtaining the experimental energy of activation for a chemical reaction. The values of $E_{\text{vis.}}$ as found by this procedure are almost constant, for normal liquids, over a range of temperature under ordinary conditions. The energy of vaporization varies only slowly with temperature, and so the ratio $\Delta E_{\text{vap.}}/E_{\text{vis.}}$ should be approximately equal to 3 or 4 in the temperature range for which $E_{\text{vis.}}$ is

* Compounds possessing very long chains present a special problem which is treated later (page 497).

¹⁹ Cf. F. Eirich and R. Simha, *J. Chem. Phys.*, **7**, 116 (1939).

constant. The results are shown in Fig. 121 in which values of $\Delta E_{\text{vap.}}$ at the boiling point are plotted as abscissae and those of $E_{\text{vis.}}$ as ordinates; lines having slopes of 3 and 4, respectively, are shown, and most of the points are seen to fall between them, as is to be expected.

It may be mentioned that the ratio $\Delta E_{\text{vap.}}/E_{\text{vis.}}$ as obtained in this manner is generally somewhat lower than n found by the method described previously. If the value of $\Delta E_{\text{vap.}}$ had been taken at a lower temperature than the boiling point the ratio would have been higher, since $\Delta E_{\text{vap.}}$ is larger under these condi-

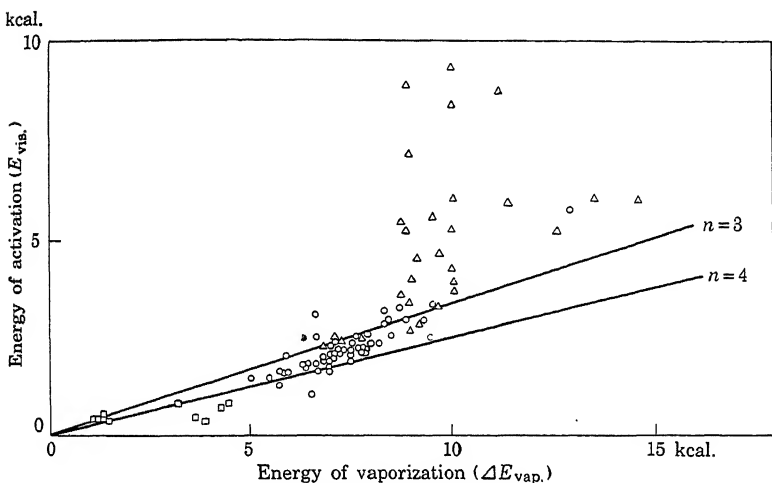


FIG. 121.—Relation between energy of activation for viscous flow and energy of vaporization. (Roseveare, Powell and Eyring.)

tions whereas $E_{\text{vis.}}$ is approximately constant. It has been shown that $\Delta E_{\text{vap.}}/E_{\text{vis.}}$ for methyl, ethyl and propyl formates, methyl, ethyl and propyl acetates and methyl propionate is 3.5 at the respective boiling points, but it increases to 4 at temperatures which are four-fifths of the boiling points.²⁰

Liquid Metals.²¹—Although most metals give linear plots of $\log \eta$ against $1/T$, the slopes differ appreciably from those of other liquids; the ratio of $\Delta E_{\text{vap.}}/E_{\text{vis.}}$ varies from 8 to 25, or more, for different metals, as compared with the normal value of 3 to 4. It appears, therefore, that the unit of flow in metals is

²⁰ Eirich and Simha, Ref. 19.

²¹ Ewell and Eyring, Ref. 4.

much smaller than the unit of vaporization; since the latter is the neutral atom, it seems probable that the former is the metal ion stripped of its conductance electrons. If this view is correct, then the following relationship may be expected to hold,

$$\frac{\Delta E_{v_i}}{E_{vis.}} \times \frac{\text{volume of ion}}{\text{volume of atom}} \quad 3 \text{ to } 4, \quad (60)$$

or, if the atoms and ions have spherical symmetry,

$$\frac{\Delta E_{v_i}}{E_{vis.}} \times r_{ion} \approx 3 \text{ to } 4, \quad (61)$$

where r_{ion} and r_{atom} refer to the radii of the ion and atom, respectively. The experimental data, which are not too reliable for the energies of vaporization, are given in Table LXII; for the polyvalent metals mercury, tin and lead the ions were assumed to be Hg^+ , Sn^{++} and Pb^{++} , respectively.

TABLE LXII.—CORRECTED RATIO OF ENERGIES OF VAPORIZATION AND ACTIVATION FOR FLOW OF METALS

Metal	Average temp., °C.	$\Delta E_{vap.}$, kcal.	$E_{vis.}$, kcal.	$\frac{\Delta E_{vap.}}{E_{vis.}}$	$\frac{\Delta E_{vap.}}{E_{vis.}} \left(\frac{r_{ion}}{r_{atom}} \right)^3$
Na	500	23.4	1.45	16.1	2.52
K	480	19.0	1.13	16.7	3.41
Ag	1400	60.7	4.82	12.5	3.79
Zn	850	26.5	3.09	8.6	2.10
Cd	750	22.5	1.65	13.5	3.96
Ga	800	34.1	1.13	30.3	2.53
Pb	700	42.6	2.80	15.9	4.97
Hg	250	13.6	0.65	20.8	2.37
Hg	600	12.3	0.55	22.2	3.54
Sn	600	15.3	1.44	10.6	4.07
Sn	1000	14.5	1.70	8.6	3.30

Although the results in the last column show some variation, it is quite evident that they are generally within or close to the range 3 to 4. It is important to point out that with metals the energy of vaporization probably cannot be so definitely interpreted as the work required to make a hole the size of an atom as is in the case of nonmetallic liquids; nevertheless, the qualitative concept of the metal ions flowing free of conductance electrons

is of interest and is in harmony with modern ideas concerning the structure of metals.²²

Long-chain Hydrocarbons.²³—Although the activation energy for viscous flow is approximately one-quarter of the heat of vaporization of a series of paraffin hydrocarbons, at least up to $C_{18}H_{38}$, a closer examination of the results shows their significance to be more important than is at first evident. If the heats of vaporization are plotted against the number of carbon atoms in the chain, the values for the first eight hydrocarbons fall on a straight line; but with increasing chain length increasing divergences are observed. It is probable that, on account of the

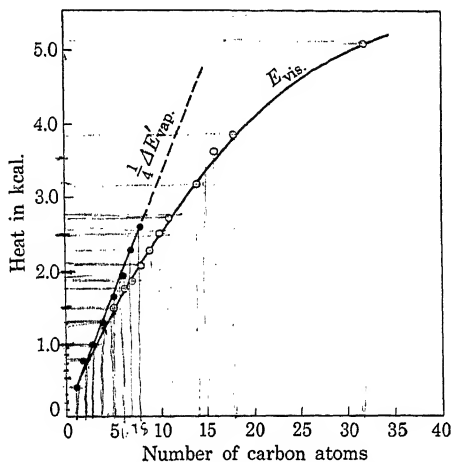


FIG. 122.—Relation between energy of activation for viscous flow and extrapolated heat of vaporization with increasing chain length. (Kauzmann and Eyring.)

tendency of the longer chains to become coiled, one-quarter of the heat of vaporization is no longer a measure of the energy required for the formation of a hole for a molecule to flow into. It is reasonable, therefore, to assume, if the hydrocarbon chain moved as a single unit, that the work required to form a hole would be one-quarter of the *extrapolated* heat of vaporization ($\Delta E'_{vap.}$), based on a linear relationship between this quantity and the number of atoms in the chain. The values of $\frac{1}{4} \Delta E'_{vap.}$ are plotted in Fig. 122, the dotted portion representing the

²² See, however, N. F. Mott and R. W. Gurney, *Rep. Progress Phys., Physical Soc. London*, **5**, 46 (1938).

²³ W. Kauzmann and H. Eyring, *J. Am. Chem. Soc.*, **62**, 3113 (1940).

extrapolated region, together with the experimental data for the activation energy for viscosity $E_{\text{vis.}}$. It is seen that for the shorter hydrocarbons the two quantities coincide, so that these substances behave normally, the whole chain being the unit of flow; as the number of carbon atoms increases, however, the values of $\frac{1}{4} \Delta E'_{\text{vap.}}$ and of $E_{\text{vis.}}$ diverge. This result suggests that as the molecules get longer they commence to move in sections rather than in single units; the work required to form a hole for the unit of flow is thus less than the $\frac{1}{4} \Delta E'_{\text{vap.}}$ that would be necessary if the unit consisted of the whole molecule.

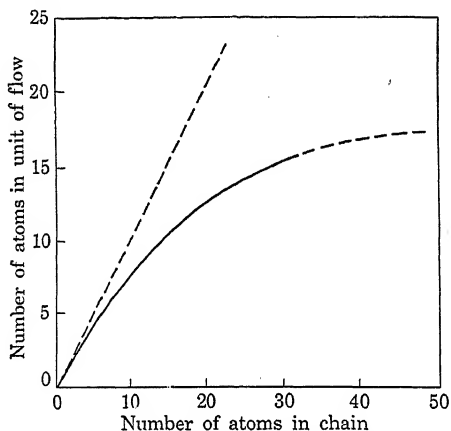


FIG. 123.—Relation between length of chain and length of unit of flow. (*Kauzmann and Eyring.*)

If the work done in forming a hole for the actual unit of flow is assumed to be one-quarter of that required for a molecule of the same size, *i.e.*, $\Delta E'_{\text{vap.}}$, it is possible to estimate the average length of the unit of flow from Fig. 122. For any value of the heat term, *i.e.*, the ordinate, the abscissa corresponding to $E_{\text{vis.}}$ gives the actual number of carbon atoms in the chain, whereas that corresponding to $\frac{1}{4} \Delta E'_{\text{vap.}}$ gives the average number of carbon atoms in the unit of flow. The results obtained in this manner are shown in Fig. 123; the dotted line shows the plot that would be obtained if the whole chain were the unit of flow. It is evident that with increasing chain length the flow unit becomes a decreasing proportion of the whole chain, and in very long chains the unit attains an average length that is approximately constant and contains 20 to 25 carbon atoms.

The activation energy of flow for such a unit, estimated from the value of $\frac{1}{4} \Delta E'_{\text{vap.}}$, is 6 to 7 kcal.

It will be seen shortly (page 510) that the number of holes in a liquid is proportional to $(V - V_s)/V_s$; and for substances, such as hydrocarbons, for which the fluidity is determined almost entirely by the number of holes, it follows that

$$\frac{V - V_s}{V_s} = c\phi, \quad (62)$$

where c is a constant and V and V_s have the same significance as on page 487. The molar volume of a solid hydrocarbon is probably closely proportional to its molecular weight, so that V may be put equal to Mv_0 , where v_0 is a constant specific volume for all solid long-chain paraffins and M is the molecular weight; further, if v_l is the specific volume of any liquid hydrocarbon, its molar volume V is equal to Mv_l , and hence Eq. (62) can be written

$$\frac{v_l - v_0}{v_0} = c\phi; \quad (63)$$

$$\therefore v_l - a = b\phi, \quad (64)$$

where a and b are constants for all long-chain paraffins. If the fluidity of a hydrocarbon depends only on the number of holes present in the liquid, it follows from Eq. (64) that the plots of the specific volume of any hydrocarbon against its fluidity should fall on one straight line, irrespective of the temperature and pressure. This is found to be the case for paraffins containing up to 14 carbon atoms in the chain; but for longer chains the observed fluidity is less, *i.e.*, the viscosity is greater, than would be required by the relationship of Eq. (64). The increase in viscosity over the expected value with long chains is also evident from the fact that up to about $\text{C}_{12}\text{H}_{26}$ the viscosity at the melting point has the approximately constant value of 0.02 poise (*cf.* page 498); but with longer chains the viscosity is in excess of this figure. The explanation of this behavior, which is developed more fully below, is connected with the suggestion that the unit of flow is smaller than the whole chain; for the molecule to flow, it is necessary for the movements of all the units or segments to be coordinated, and the probability of this occurring will decrease as the length of the whole chain increases. The consequence

will be a higher viscosity than would be the case if all the units moved together automatically.

Long-chain Polymers.—Studies of the viscosities of a number of linear polyesters have brought to light the interesting fact that the activation energies of flow are very low, about 8 kcal., considering the average length of the molecules present in the system, and further that the values are almost independent of the molecular weights of the polymers. The results are in harmony with the view expressed above that in very long molecules the unit of flow is a segment of approximately constant length; the actual length of the unit can be estimated in the following manner. According to P. J. Flory²⁴ the viscosities of the linear polyesters may be expressed in terms of the "weight average chain length" Z , which is a measure of the average number of atoms in a chain, by an equation that can be put in the form

$$\ln \eta = \frac{A}{R} + \frac{B}{R} Z^{1/2} + \frac{C}{RT}, \quad (65)$$

where R is the gas constant and A , B and C are constants for a series of polymers, independent of temperature. This equation may be compared with Eq. (28) written as

$$\ln \eta = \ln \frac{Nh}{V} - \frac{\Delta S^\ddagger}{R} + \frac{\Delta H^\ddagger}{RT}, \quad (66)$$

so that C may be identified with ΔH^\ddagger and ΔS^\ddagger can be related to A , B and Z . Some of the values of A , B and C (or ΔH^\ddagger) for a

TABLE LXIII.—VISCOSITY CONSTANTS OF LINEAR POLYESTERS

Polymer unit	n	A	B	ΔH^\ddagger , kcal.
$-\text{O} \cdot (\text{CH}_2)_{10} \cdot \text{O} \cdot \text{CO} \cdot (\text{CH}_2)_6 \cdot \text{CO}-$	8	-27.8	0.510	8.05
$-\text{O} \cdot (\text{CH}_2)_{10} \cdot \text{O} \cdot \text{CO} \cdot (\text{CH}_2)_4 \cdot \text{CO}-$	7	-28.3	0.527	8.23
$-\text{O} \cdot (\text{CH}_2)_{10} \cdot \text{O} \cdot \text{CO} \cdot (\text{CH}_2)_2 \cdot \text{CO}-$	6	-28.9	0.516	8.55
$-\text{O} \cdot (\text{CH}_2)_2 \cdot \text{O} \cdot (\text{CH}_2)_2 \cdot \text{O} \cdot \text{CO} \cdot (\text{CH}_2)_4 \cdot \text{CO}-$	5	-27.8	0.457	8.40

number of polyesters are given in Table LXIII; n is the number of methylene groups per $-\text{CO} \cdot \text{O}-$ group in the chain. It is seen that A is approximately -28, B is about 0.5 and ΔH^\ddagger is in the

²⁴ P. J. Flory, *ibid.*, 62, 1057 (1940).

vicinity of 8 kcal. for all the substances under consideration. If the work required to produce a hole for the molecule to flow into is one-quarter of the heat of vaporization, the value of the latter is about 32 kcal. The heats of vaporization of simple esters containing the same number of methylene groups per $-\text{CO}\cdot\text{O}-$ group as do the polyesters are known; and hence the number of atoms, including oxygen atoms, in the unit of flow can be calculated by proportion. The numbers obtained in this manner are 34, 33, 30 and 28 atoms, respectively; it follows, therefore, that there are approximately 32 atoms in each segment of flow. The molecular weight of a segment is thus about 500, and hence its molar volume V in Eq. (66) may be supposed to have the same value; if the mean values of A and B given above are used, it follows from Eqs. (65) and (66) that

$$\Delta S^\ddagger = 6.8 - 0.5Z^{1/2}. \quad (67)$$

It is seen, therefore, that in activation a moving unit gains 6.8 e.u., less an amount depending on the average length of the whole molecule.²⁵

In spite of the fact that the moving segments have approximately the same length and that the activation energy is almost the same in each case, it is seen from Eq. (65) that the viscosity depends on the total chain length. Although the flow of a long chain is believed to be merely the resultant of the motion of segments of definite size that jump from one equilibrium position to another at a given rate, independent of how many segments are joined together in the chain, it is necessary that there should be some coordination of the movement of the segments if the chain as a whole is to progress. The fraction of successful jumps, which determines the actual fluidity of the polymer, should be independent of temperature but should be a function of the amount of cooperation of the segments constituting the chain, whereas the total number of jumps in unit time depends on the size and nature of the segments and on the temperature and pressure; thus,

$$\phi = F(Z)G(p, T'), \quad (68)$$

where the function F may be taken as the same for all linear molecules, assuming the same type of cooperation to be neces-

²⁵ Kauzmann and Eyring, Ref. 23.

sary, and the function G depends on the nature of the polymer. According to Eq. (67), $F(Z)$ is of the form $e^{-aZ^{1/2}}$, where a is equal to B/R and has approximately the value $0.5/2$, i.e., 0.25 . Since e^{-x} becomes equal to $[1 - (x/n)]^n$ when n is large and very much greater than x , it follows that

$$F(Z) = e^{-aZ^{1/2}} \approx \left(1 - \frac{a}{n} Z^{1/2}\right)^n. \quad (69)$$

The quantity on the extreme right of this equation is, mathematically, the probability that n successive and independent events, each having a probability $(1 - aZ^{1/2}/n)$ of success, shall all be successful. The experimental facts are, therefore, in agreement with the view that the fluidity is related to the probability of the coordinated movement of all the segments constituting a long chain.

According to the foregoing deduction the probability of failure of any unit to move in coordination with the others is given by Eq. (69) as $aZ^{1/2}/n$, and the following considerations provide a theoretical basis for this result.²⁶ A freely twisting hydrocarbon molecule containing Z links encloses an average volume of $3.4Z^{3/2} \times 10^{-24}$ cc., while the chain itself occupies a volume V_2 of $20Z \times 10^{-24}$ cc.²⁷ Of the total volume enclosed by the freely twisting chain containing n segments, the portion V_1 , equal to $\frac{1}{n} (3.4Z^{3/2})$, is available for each segment. In order that movement may be successful the segment must be located within some definite region of the volume V_2 that the molecule will occupy after moving under the action of the shear force. The probability of failure is the probability that the segment shall be in the portion V_1 of the total space $V_1 + V_2$ in which it might be, and this is given by

$$\frac{V_1}{V_1 + V_2} \approx \frac{V_1}{V_2} = \frac{3.4}{20n} Z^{1/2} = \frac{0.17}{n} Z^{1/2}, \quad (70)$$

which is in agreement with the result given above. The value of the constant a derived in this manner is 0.17 , compared with the experimental result of 0.25 for the linear polyesters. It should be noted that a may be expected to be almost independ-

²⁶ Kauzmann and Eyring, Ref. 23.

²⁷ W. Kuhn, *Kolloid-Z.*, **76**, 258 (1936).

ent of the nature of the straight chain, and the approximation of taking it to be equal to 0.25, *i.e.*, B is 0.5, in other cases will be made below.

Liquid Sulfur.²⁸—It is well known that the viscosity of liquid sulfur, which increases normally with increasing temperature just above its melting point, undergoes a marked increase at about 160 and 190°C. At still higher temperatures, the variation of viscosity with temperature is normal once again.²⁹ From the experimental results the activation energy for viscous flow below 160°C. is found to be 7.04 kcal. It is probable that the sulfur molecule, as in the solid state, consists of puckered rings of formula S_8 , and the ratio of $\Delta E_{\text{vap.}}/E_{\text{vis.}}$ may be expected to be approximately 3, as for cyclohexane. The value of $\Delta E_{\text{vap.}}$ at 120°C. has been found to be 2.59 kcal. per g.-atom³⁰; and hence, for the S_8 molecule, $\Delta E_{\text{vap.}}$ should be 20.7 kcal. In the range 90 to 160°C., $E_{\text{vis.}}$ is 7.04 kcal., as seen above; and hence $\Delta E_{\text{vap.}}/E_{\text{vis.}}$ is approximately 3, in agreement with expectation.

Above 250°C. the temperature coefficient indicates a higher activation energy than below 160°C.; the actual values depend, however, on whether the measurements are made during heating or cooling. In any case the relatively high activation energy shows that the unit of flow is now larger than at the lower temperatures; this unit might be either a large ring or a chain, and of these possibilities the latter seems more likely to be correct. It is probable that while the temperature of the liquid is being raised some of the sulfur—sulfur bonds are being broken, so that part of the apparent activation energy for flow is due to this factor. On cooling, however, the recombination process takes place slowly, and the heat of activation obtained under these conditions represents more closely the true value for flow. The viscosity measurements then indicate that $E_{\text{vis.}}$ is about 10 kcal., and so, on the assumption that $\Delta E_{\text{vap.}}/E_{\text{vis.}}$ is equal to 4, as would be expected for a long-chain substance, the heat of vaporization of the unit of flow will be 40 kcal. The experimental heat of vaporization at 350°C., in the region of which the viscosity measurements were made, is 2.05 kcal. per g.-atom;³¹

²⁸ Kauzmann and Eyring, Ref. 23; Ewell and Eyring, Ref. 4.

²⁹ L. Rotinjanz, *Z. physik. Chem.*, **62**, 609 (1908).

³⁰ W. A. West and A. W. C. Menzies, *J. Phys. Chem.*, **33**, 1880 (1929).

³¹ West and Menzies, Ref. 30.

and so it may be concluded that the segment of flow contains $40/2.05$, *i.e.*, about 20, sulfur atoms. The total average length of the chain of sulfur atoms may be calculated approximately from the entropy of activation; it being assumed that the entropy of the flow segment is small, Eq. (67) can be reduced to the form

$$\Delta S^\ddagger = -0.5Z^{1/2}, \quad (71)$$

and so the weight average length of the chain can be calculated directly from the entropy of activation. The constant B , equal to 0.5, has been taken with some justification (page 502) to be the same as for the linear polyesters for which Eq. (65) was proposed. Since the heat of activation for flow is known, the corresponding entropy may be derived from the viscosity and the molar volume by means of Eq. (28); this is found to be -37 E.U. in the case of sulfur, so that Z , the weight average length of the sulfur chain, is about 5,500 atoms. If the viscosity measurements obtained while the temperature of the liquid was being raised had been used, $E_{\text{vis.}}$ would be 18.35 kcal.; and hence, by the arguments used above, the unit of flow would be 36 sulfur atoms long. The entropy of activation under these conditions is calculated as -55 E.U., and the weight average length of the whole chain of sulfur atoms would be 12,000. At any temperature, there is probably an equilibrium mixture of chains of varying length, and as the temperature is raised the average chain length will become smaller.

It has been suggested that the increase in viscosity of liquid sulfur above 160°C. is due to the breaking of the S_8 rings and the formation of relatively short irregular chains which tangle with one another.³² The idea of long sulfur chains, however, seems more probable, especially in view of the fact that sudden cooling of the liquid leads to the formation of plastic sulfur which is known to have a fiberlike structure.

Associated Liquids.³³—The behavior of associated liquids, such as hydroxylic compounds, is abnormal in several respects; the viscosities are very much higher than for analogous nonassociated

³² B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, **3**, 6 (1935); see also N. S. Gingrich, *ibid.*, **8**, 29 (1940).

³³ Ewell and Eyring, Ref. 4.

substances, and the values decrease rapidly with increasing temperature. The plot of $\log \eta$ against $1/T$ is not linear, and hence the energy of activation for viscous flow is not independent of temperature. The results for water are given in Table LXIV, the value of the ratio $\Delta E_{\text{vap.}}/E_{\text{vis.}}$ being included; it is seen to increase from 2.0 to 3.9 as the temperature is increased from 0° to 150°c.

TABLE LXIV.—VISCOSITY DATA FOR WATER

Temp., °c.	η , millipoises	$E_{\text{vis.}}$, kcal.	$\Delta E_{\text{vap.}}$, kcal.	$\frac{\Delta E_{\text{vap.}}}{E_{\text{vis.}}}$
0	17.95	5.06	10.18	2.01
50	5.49	3.42	9.61	2.81
100	2.84	2.80	8.98	3.20
150	1.84	2.11	8.28	3.90

The relatively high value of $E_{\text{vis.}}$ at 0°, which is about twice that expected, is to be attributed to the fact that, in addition to the normal work required to make a hole, it is necessary for the hydrogen bonds, whereby a water molecule is attached to the surrounding molecules, to be broken before the activated state for flow can be attained. There is consequently what might be termed a "structure activation energy," in addition to the normal activation energy, for the flow of water and other associated liquids. As the temperature is raised, there is a decrease in the number of hydrogen bonds that have to be broken before flow can occur, and hence the activation energy decreases; the value observed for water at 150°c. is probably free from any appreciable contribution due to structural changes. The high activation energy for the flow of water and other associated liquids accounts for the high viscosities of these substances. When the compound contains two or more hydroxyl groups, as in glycerol and glycol, for example, the viscosity is very high on account of the relatively large number of hydrogen bonds which must be broken in the formation of the activated state for flow.

Entropy of Activation for Flow.—In view of the high activation energy for flow of associated liquids, it is a striking fact that the free energy of activation shows no such abnormality (page 492).

The explanation is that ΔF^\ddagger is equivalent to $\Delta H^\ddagger - T \Delta S^\ddagger$ and that the high value of the heat of activation ΔH^\ddagger is compensated by the large positive value of ΔS^\ddagger , so that ΔF^\ddagger remains normal. If, as suggested above, the unit of flow even in associated liquids is a single molecule and the formation of the activated state involves the breaking of a number of hydrogen bonds, it is evident that the entropy of the activated state will be appreciably greater than that of the initial state. In other words, the entropy of activation for flow ΔS^\ddagger should be relatively large and positive, in agreement with the experimental fact that ΔF^\ddagger is normal in spite of the high value of ΔH^\ddagger for associated liquids.

It has been seen above that for molecules of spherical, or approximately spherical, symmetry, $\Delta E_{\text{vap.}}/E_{\text{vis.}}$ is about 3, compared with a value of 4 for nonspherical substances; this means that the energies of activation for flow are relatively large for the former, and hence, in accordance with the conclusions just reached for associated liquids, the entropy of activation for flow should be comparatively high. This is in agreement with observation and suggests, as might be expected, that the symmetrical molecules are well packed in the normal liquid state. Among the molecules for which n is 3, mention may be made of nitrogen, oxygen, carbon monoxide and argon, which probably have a close-packed spherical structure in the liquid, and of benzene, naphthalene and cyclohexane.

Influence of Pressure on Viscosity.³⁴—In the derivation of the viscosity equations given above, the use of $E_{\text{vis.}}$ for the activation energy for flow involved the assumption that in the formation of the hole for a molecule to flow into no appreciable work was done against the external pressure. In view of the fact that the viscosity of a liquid varies with the pressure at constant temperature, it is evident that the production of a hole is accompanied by an increase in the total volume of the system. If ΔV represents this increase of volume per mole of activated state for flow, *i.e.*, for a mole of holes, then, at constant external pressure p ,

$$E_{\text{act.}} = E_{\text{vis.}} + p \Delta V. \quad (72)$$

The quantity ΔV will be some fraction of the molar volume V , so

³⁴ Ewell and Eyring, Ref. 4; D. Frisch, H. Eyring and J. F. Kincaid, *J. App. Phys.* **11**, 75 (1940).

that ΔV may be replaced by V/n' ; hence,

$$E_{\text{act.}} = E_{\text{vis.}} + \frac{pV}{n'} \quad (73)$$

$$= \frac{\Delta E_{\text{vap.}}}{n} + \frac{pV}{n'}, \quad (74)$$

$\Delta E_{\text{vap.}}/n$ being written for $E_{\text{vis.}}$ as on page 493; Eq. (32) may now be expressed in the form

$$\eta = \frac{N}{V} (2\pi mkT)^{1/2} v_f^{1/2} e^{(\Delta E_{\text{vap.}}/n + pV/n')/RT}. \quad (75)$$

In order to determine the quantity n' , representing the ratio of the increase of volume accompanying flow to the total volume, the method adopted is to use the experimental value of η obtained at low pressure, together with the known energy of vaporization $\Delta E_{\text{vap.}}$ and the free volume v_f derived from the measured velocity of sound in liquid and gas (page 479), and so to determine n from Eq. (75). The term involving pV/n' is neglected, since p is small, and the method is virtually identical with that described on page 493. The value of n obtained in this way is now employed together with the experimental data for η at high pressures to calculate n' from the complete equation (75) at various pressures and temperatures. The energies of vaporization must in all cases be corrected to the particular pressure by means of the available P - V - T data for the liquid. The calculations have been carried out for a number of substances; the results for all the cases studied, except for water, which behaves in an exceptional manner, are given in Table LXV.³⁵

TABLE LXV.—VALUES OF n' FOR NORMAL LIQUIDS

Pressure, kg./cm. ²	n-Pentane (30°C.)	Diethyl ether (52.6°C.)	Benzene (25°C.)	Isopentane (50°C.)	Mercury (0°C.)
1,000	6.0	...	5.5	8.0
2,000	6.9	4.7	25.0
4,000	8.5	6.0	23.0
6,000	9.7	6.8	21.2
8,000	10.4	7.2
10,000	10.8	7.6

³⁵ Data from Bridgman, Ref. 11.

It is evident that n' is approximately independent of pressure, and the results, except for metals and associated liquids, fall within the range of about 6 to 8. By taking a mean value of n' , it is possible to determine the ratio n'/n , since n is already known, for a series of substances; the results are quoted in Table LXVI.

TABLE LXVI.—COMPARISON OF n AND n' FOR LIQUIDS

Substance	n	n'	n'/n
n-Pentane.....	4.4	7.8	1.8
Diethyl ether.....	4.5	7.0	1.6
Benzene.....	3.3	5.5	1.7
Isopentane.....	4.4	8.0	1.8
Mercury.....	11	23	2.1

The constancy of the ratio n'/n for the nonmetallic liquids and the relatively small divergence in the result for mercury in spite of the large variation of n and n' are very striking; this conclusion, as well as the fact that n'/n is not unity, must have an important significance. The quantity $\Delta\epsilon_{\text{vap.}}$ is the amount of energy* required to form a hole of molecular size, and $1/n$ is the fraction of this amount expended in the formation of a hole large enough for viscous flow to occur. By the definition of n' the size of this hole is approximately a fraction $1/n'$ of a hole of molecular dimensions; it might be expected, therefore, that n'/n should not differ markedly from unity. The fact that this is not so means that the energy required to form a hole is not proportional to its size. From the results in Table LXVI, it appears that the work required to form a hole of approximately one-seventh the size of a molecule is about one-fourth the energy of vaporization per molecule. If seven of these holes are combined to form one of molecular size, energy roughly equal to $(\frac{7}{4} - 1)\epsilon_{\text{vap.}}$, i.e., $0.75\epsilon_{\text{vap.}}$, would be liberated.

By assuming n'/n to have the constant value of 1.75, it is possible to use Eq. (75) to express the variation of the viscosity of a liquid with pressure, the only data required being the energy of vaporization as a function of volume or pressure. A conven-

* $\Delta\epsilon_{\text{vap.}}$ is the energy of vaporization per molecule, i.e., $\Delta E_{\text{vap.}}/N$, where N is the Avogadro number.

lent relationship is $\partial E/\partial V = (\alpha/\beta)T - p$, where α and β are the coefficients of thermal expansion and of compressibility, respectively. The calculations have been made for a range of pressures for ethyl ether, mercury and n-pentane, and the results are depicted graphically, together with the experimental data, in Fig. 124; the agreement between observed (full lines) and calculated (dotted lines) values is satisfactory, and so it is possible to predict with fair accuracy the influence of pressure on the viscosity of normal liquids.

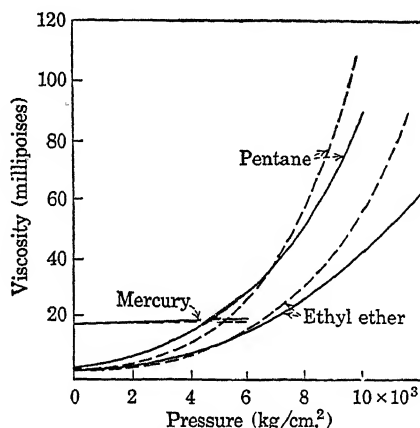


FIG. 124.—Observed and calculated variation of viscosity with pressure. (Frisch, Eyring and Kincaid.)

The behavior of water in relation to Eq. (75) is exceptional; the value of n' is not independent of pressure, the results for 0°C. being given in Table LXVII for different values of n . The

TABLE LXVII.—VALUES OF n' FOR WATER AT 0°C.

Pressure, kg./cm. ²	$n = 2$	$n = 4$	$n = 5.4$
1,000	16.1	124
2,000	32	16	14
3,000	19	11	9.7
4,000	14	8.8	8.0
5,000	10.6	7.7	7.2

decrease of n' with increasing pressure may be attributed to changes in the structure of water. It is probable that at low pressures water has a four-coordinated open structure, and no

appreciable extra volume is required for flow to occur, *i.e.*, n' is large. As the pressure is increased, the open structure presumably collapses, and at high pressures the activated state requires the same fraction of the molecular volume for flow as a non-hydroxylic compound. The value of n' approaches a constant at high pressures, and it is of interest to note that for reasonable values of n , *viz.*, 4 to 5, the fraction n'/n is slightly less than 2, as is the case with normal liquids. A similar type of behavior might be expected for alcohol and other substances in which hydrogen bonds occur in the solid state.

The number of holes n_h per mole of liquid is equal to $(V - V_s)/v_h$, where V and V_s are the molar volumes of liquid and unexpanded solid, respectively, and v_h is the increase in volume required to form a single hole. If v_s , *i.e.*, V_s/N , is the volume of a single molecule, according to the argument on page 487, then v_h is equivalent to v_s/n' , *i.e.*, V_s/Nn' , and hence

$$n_h = \frac{V - V_s}{V_s} Nn'; \quad (76)$$

$$\therefore \frac{n_h}{N} = \frac{V - V_s}{V_s} n'. \quad (77)$$

It was seen on page 489 that for many simple substances n_h/N at the melting point is equal to 0.54, and hence

$$n' \frac{V_m - V_s}{V_s} = 0.54, \quad (78)$$

where V_m is the molar volume of the liquid at the melting point. For a number of nonmetallic substances, $(V_m - V_s)/V_s$ is approximately 0.1, and hence n' is about 5 or 6, in general agreement with the results in Table LXVI. For mercury, sodium, potassium, rubidium and cesium, $(V_m - V_s)/V_s$ is about 0.25, and so n' , as found above for mercury, is in the vicinity of 25.³⁶

Viscosity in Unimolecular Films.³⁷—The equations already derived for the flow of three-dimensional liquids may be modified so as to be applicable to the viscosity of surface films, *i.e.*, when movement is possible in two dimensions only. The shearing force acting on a single molecule at the interface is now $f\lambda_2$; and since this acts over a distance $\frac{1}{2}\lambda$, the energy of activation

³⁶ Powell, Roseveare and Eyring, Ref. 9.

³⁷ W. J. Moore and H. Eyring, *J. Chem. Phys.*, 6, 391 (1938).

for movement of a molecule in the forward direction is diminished by $\frac{1}{2}f\lambda_2\lambda$, whereas it is increased by a similar amount for movement in the opposite direction. It follows, therefore, according to the discussion on page 483, that

$$\Delta u = \lambda k(e^{\frac{1}{2}f\lambda_2\lambda/kT} - e^{-\frac{1}{2}f\lambda_2\lambda/kT}), \quad (79)$$

and on expansion by making the assumption that $2kT \gg f\lambda_2\lambda$ and utilizing the appropriate value of k , it is found that

$$\eta = \frac{\lambda_1 h}{\lambda_2 \lambda^2} \cdot \frac{F}{F_{\ddagger}} e^{e_0/kT} \quad (80)$$

If, as an approximation, λ is put equal to λ_1 the result is

$$\eta = \frac{h}{\lambda_2 \lambda_1} \cdot \frac{F}{F_{\ddagger}} e^{e_0/kT}, \quad (81)$$

or, alternatively,

$$\eta = \frac{h}{\lambda_2 \lambda_1} e^{\Delta F^{\ddagger}/RT}. \quad (82)$$

Upon adopting the same procedure as before, $\lambda_2\lambda_1$ may be put equal to the cross-sectional area of the units taking part in two-dimensional flow; if these may be identified with the molecules, $\lambda_2\lambda_1$ may be replaced by A/N , where A is the cross-sectional area per mole. It is thus possible to write

$$\eta = \frac{hN}{A} e^{\Delta F^{\ddagger}/RT}, \quad (83)$$

which is the two-dimensional analogue of Eq. (27). The values of ΔF^{\ddagger} , the free energy of activation for flow in a unimolecular film, have been computed from experimental data of surface viscosity, and the results are compared in Table LXVIII with

TABLE LXVIII.—COMPARISON OF FREE ENERGIES OF ACTIVATION FOR TWO- AND THREE-DIMENSIONAL FLOW

Substance	ΔF^{\ddagger} for film, kcal.	ΔF^{\ddagger} for liquid, kcal.	Ratio
Myristic acid.....	10.36	5.77 (70°)	1.80
Palmitic acid.....	10.90	5.92	1.84
Stearic acid.....	11.03	6.30	1.75
Oleic acid.....	10.36	6.22 (20°)	1.67
Cetyl alcohol.....	15.20	5.80	2.62

the values for viscous flow in the same three-dimensional liquids. The free energy of activation for flow is approximately two to three times as great in the surface layer as it is in the liquid in bulk; it is probable, therefore, that the unit of flow is somewhat greater in the former circumstances. This may be due to the lateral association of the hydrocarbon chains of the surface molecules or to solvation of the polar groups. If the latter, each molecule of liquid spread on the surface would have to drag with it a number of molecules of the underlying liquid in the process of flow. In any event, the free energy of activation would be greater than for the three-dimensional flow in the pure liquid.

Compression of the unimolecular surface film, *i.e.*, by increasing the surface pressure, is comparable with increase of external pressure for liquid viscosity. Upon rewriting Eq. (83) and splitting up ΔF^\ddagger into ΔH^\ddagger and the entropy term, it is readily seen that

$$\eta = B e^{\Delta H^\ddagger/RT}, \quad (84)$$

provided that ΔS^\ddagger is assumed to be constant. The quantity ΔH^\ddagger may be replaced by $\Delta E^\ddagger + p \Delta A$, allowance being made for the fact that there is an expansion ΔA in the formation of the activated state, so that external work must be done against the surface pressure; by identifying ΔE^\ddagger with the experimental activation energy $E_{\text{vis.}}$ for surface viscosity at zero pressure, Eq. (84) becomes

$$\eta = B e^{(E_{\text{vis.}} + p \Delta A)/RT} \quad (85)$$

$$= B e^{E_{\text{vis.}}/RT} e^{p \Delta A/RT}. \quad (86)$$

If the quantity $B e^{E_{\text{vis.}}/RT}$, which is the surface viscosity at zero pressure, is designated as η_0 , it follows that

$$\eta = \eta_0 e^{p \Delta A/RT}, \quad (87)$$

or

$$\ln \eta = \ln \eta_0 + \frac{p \Delta A}{RT}. \quad (88)$$

If ΔA may be taken as constant for a given substance and independent of pressure, as will probably be the case over a considerable range of surface pressure, it follows that

$$\log \eta = \log \eta_0 + pc, \quad (89)$$

where c is a constant. The general accuracy of this equation has been confirmed by the experimental work on surface films of E. Boyd and W. D. Harkins;³⁸ further, the observed magnitude of the constant c is in agreement with the expected value. It may be seen from Eq. (88) that c is equivalent to $\Delta A/RT$; and if ΔA is taken to be equal to the area of cross section of a single hydrocarbon chain multiplied by the Avogadro number, c is found to be 0.054 at 25°C. The experimental values range between 0.022 and 0.076.

Non-Newtonian Flow.³⁹—It has been seen that, provided $2kT \gg f\lambda_2\lambda_3\lambda$, the quantity f disappears from the viscosity equation; the viscosity is thus independent of the shearing force, as required for a Newtonian liquid. If the structure of the system is fairly rigid, as is the case with certain gels, lyophilic sols and glasses, the value of f must be large and hence $f\lambda_2\lambda_3\lambda$ becomes greater than $2kT$; in these circumstances,

$$\sinh \frac{f\lambda_2\lambda_3\lambda}{2kT} \approx e^{\frac{1}{2}f\lambda_2\lambda_3\lambda/kT}, \quad (90)$$

provided that $f\lambda_2\lambda_3\lambda$ is approximately equal to, or greater than, $2kT$, and Eq. (22) becomes

$$\eta = \frac{f\lambda_1 h}{\lambda kT} \cdot \frac{F}{F_{\ddagger}} e^{(\epsilon_0 - \frac{1}{2}f\lambda_2\lambda_3\lambda)/kT}. \quad (91)$$

This equation may be written in the form

$$\eta = Af e^{(a-bf)/T}, \quad (92)$$

where A is equal to $\lambda_1 h F / \lambda k T F_{\ddagger}$, a is ϵ_0/k and b is $\frac{1}{2}\lambda_2\lambda_3\lambda/k$. It is clear from Eq. (92) that the viscosity is now no longer independent of the shearing force, and hence the flow will be non-Newtonian.* It should be noted that, since the quantity $a - bf$ appears in the exponential term, the viscosity should decrease with increasing shearing force; this is in harmony with the experimental observations.

³⁸ E. Boyd and W. D. Harkins, *J. Am. Chem. Soc.*, **61**, 1188 (1939).

³⁹ Eyring, Ref. 1; Ewell, Ref. 4.

* Another possible interpretation of non-Newtonian flow, based on a change in structure or flow mechanism as the rate of flow changes, is considered by W. Kauzmann and H. Eyring [*J. Am. Chem. Soc.*, **62**, 3113 (1940)].

The viscosities of suspensions of raw milled rubber have been found to obey Eq. (92) closely for shearing forces from 84×10^4 to 190×10^4 dynes per sq. cm., and approximately for even larger forces, approximate values of A , a and b being determined empirically by a graphical procedure.⁴⁰ For the particular rubber system employed the best agreement with experiment was observed when the following values were used: $A = 1.65 \times 10^{-4}$, $a = 5.10 \times 10^3$ and $b = 1.28 \times 10^{-3}$. Since a is equal to ϵ_0/k , where ϵ_0 is the activation energy for flow of a single unit when the shearing force is small, the corresponding energy per "mole" is given by aR , where R is the gas constant. It follows, therefore, that $E_{\text{vis.}}$ for raw milled rubber is $5.1 \times 10^3 \times 2$, i.e., 10.2 kcal. If the unit of flow is chainlike in form, its heat of vaporization will be four times this quantity (cf. page 497), i.e., 40.8 kcal. The chains in rubber presumably consist of a number of isoprene residues; and since the molar heat of vaporization of isoprene is 4 kcal., it is probable that the segment of flow consists of about 10 residues. Each molecule of isoprene contains a chain of four carbon atoms, and so the unit of flow is a chain of approximately 40 carbon atoms. The entropy of activation for flow is calculated to be -42 E.U., by means of Eq. (28); and, by utilizing the simplified equation (71) for the relationship between ΔS^\ddagger and the weight average total chain length, the latter in raw milled rubber is found to be about 7,000 carbon atoms.⁴¹

The factor b in Eq. (92) is equivalent to $\frac{1}{2}\lambda_2\lambda_3\lambda/k$; and since b for raw milled rubber is 1.28×10^{-3} , it follows that the "viscous volume" $\lambda_2\lambda_3\lambda$ is equal to 3.5×10^{-19} cc. According to the calculations made above the segment of flow consists of 40 carbon atoms, and so its length is about 50×10^{-8} cm. The diameter of the chain is about 5×10^{-8} cm.; and if the distance moved by a segment in each jump is approximately the same, the viscous volume might be expected to be 1.25×10^{-21} cc., which is much smaller than the experimental value. An explanation of this discrepancy is probably that a small section of the rubber molecule resists the shear on a large area.

Viscosity of Mixtures.—Numerous attempts have been made to derive an equation relating the viscosity of a mixture to its

⁴⁰ H. M. Smallwood, *J. App. Phys.*, **8**, 505 (1937); data from M. Mooney, *Physics*, **7**, 413 (1936).

⁴¹ Kauzmann and Eyring, Ref. 23.

composition and the viscosities of its constituents, but none can be regarded as satisfactory, especially for liquid systems exhibiting appreciable departure from ideal behavior.⁴² If viscous flow consists of the movement of one molecule at a time from one equilibrium position to the next, then provided that the two molecular species in a mixture do not interact with one another, *i.e.*, for an ideal system, it can be shown from Eqs. (14) to (21), on the assumption that the λ 's are the same for both constituents, that

$$\phi = N_1\phi_1 + N_2\phi_2, \quad (93)$$

where ϕ is the fluidity of the mixture and ϕ_1 and ϕ_2 are the values for the two constituents, whose mole fractions are N_1 and N_2 , respectively. It will be noted, however, that Eq. (93) involves the tacit assumption that the free energy of activation, which as already seen is a definite fraction of the energy required to make a hole for the molecule to flow into, is the same in the mixture as in the pure liquids. It is unlikely that this will be the case, and it is more reasonable to take an average value, *viz.*, $N_1 \Delta F_1^\ddagger + N_2 \Delta F_2^\ddagger$, as applicable to the mixture. Since Eq. (27) for a pure substance may be written as

$$\phi = (V/hN) e^{-\Delta F^\ddagger/RT},$$

an analogous equation for the fluidity of a mixture would be

$$\phi = \frac{V_{1,2}}{hN} e^{-(N_1\Delta F_1^\ddagger + N_2\Delta F_2^\ddagger)/RT}, \quad (94)$$

where $V_{1,2}$ is the average molar volume of the components. It is of interest to note that if V_1 and V_2 are not very different, $V_{1,2}$ will have approximately the same value; Eq. (94) can then be written in the form

$$\log \phi = N_1 \log \phi_1 + N_2 \log \phi_2, \quad (95)$$

which is the equation proposed by J. Kendall.⁴³

A test of Eq. (94) has shown that it is obeyed only by mixtures of similar liquids; systems consisting of markedly dissimilar substances, *e.g.*, benzene and alcohol, have much lower viscosi-

⁴² See J. Kendall and K. P. Monroe, *J. Am. Chem. Soc.*, **39**, 1789 (1917).

⁴³ J. Kendall, *Meddel. Vetenskapsakad. Nobelinst.*, **2**, [25] (1913).

ties, and systems in which compound formation occurs, e.g., chloroform and ether, have viscosities greater than the calculated values. Comparison of the deviations of the observed free energies of activation for flow in mixtures from the linear additive law required by Eq. (94) with the deviations from Raoult's law, both at 50 moles per cent, where the departures from ideal behavior are generally a maximum, shows a close proportionality for a number of liquid systems;⁴⁴ the deviation in ΔF^\ddagger for viscosity is apparently equal to $\Delta F_m/2.45$, where ΔF_m , called the "excess free energy of mixing," represents the departure from Raoult's law.⁴⁵ It is an interesting fact, which must have important significance, that the same ratio, *viz.*, 2.45, appears here as does in connection with the relationship between ΔF^\ddagger for viscosity and the energy of vaporization, or the work required to form a hole in the liquid. If use is made of this connection between the deviation from Eq. (94) and the excess free energy of mixing, this equation may be modified, thus,

$$\phi = \frac{V_{1,2}}{hN} e^{-[(N_1 \Delta F_1^\ddagger + N_2 \Delta F_2^\ddagger) - \Delta F_m/2.45]/RT}, \quad (96)$$

or, since ΔF^\ddagger is equal to $\Delta E_{\text{vap.}}/2.45$,

$$\psi = \frac{V_{1,2}}{hN} e^{-(N_1 \Delta E_1 + N_2 \Delta E_2 - \Delta F_m)/2.45 RT}. \quad (97)$$

Equations (96) and (97) can be tested provided that the vapor pressures of mixtures are available at the desired temperatures, so that ΔF_m can be calculated. As is to be expected, since the correction term was derived empirically, the modified mixture law of Eq. (97) gives excellent agreement with experiment, even for systems consisting of a hydrocarbon and an associated substance. The observed fluidities for mixtures of benzene and phenol are shown by the circles in Fig. 125, and the full line gives values calculated by means of Eq. (97); the dotted line is for the ideal mixture law of Eq. (94).

DIFFUSION

Diffusion as a Rate Process.⁴⁶—The problem of diffusion can be treated in a manner similar to that used for viscosity, for it

⁴⁴ Powell, Roseveare and Eyring, Ref. 17.

⁴⁵ Cf. G. Scatchard, *Chem. Rev.*, **8**, 321 (1931).

⁴⁶ Eyring, Ref. 1; H. S. Taylor, *J. Chem. Phys.*, **6**, 331 (1938).

is evident that the two properties must be related. The classical treatment of diffusion in solution is based on the assumption that van't Hoff's equation $P = cRT$, relating the osmotic pressure P to the concentration c , is obeyed, that osmotic pressure is the driving force of diffusion and that Stokes's law is applicable to the movement of solute molecules. The first two assumptions are probably justifiable only in extremely dilute solutions, and the last can hold only when the diffusing molecules are very much larger than those of the medium. In spite of its limitations the resulting Stokes-Einstein equation, *viz.*,

$$D = \frac{kT}{6\pi r\eta}, \quad (98)$$

has been frequently employed; D is the diffusion coefficient defined by the relationship*

$$ds = -DA \frac{dc}{dx} dt, \quad (99)$$

where ds is the quantity of solute that crosses a boundary of cross section A in the time dt when the concentration gradient is dc/dx , the distance x being measured in the direction of diffusion. A more satisfactory treatment of diffusion in solution, which is free from the objections of the classical approach, is by means of the theory of absolute reaction rates.

The process of diffusion is very similar to that of viscous flow, except that in the former case unlike molecules are involved. In order to diffuse in solution, a molecule of solute and one of solvent are required to slip past each other. Suppose the distance between two successive equilibrium positions is λ ,† so that this is the distance through which a molecule of solute is

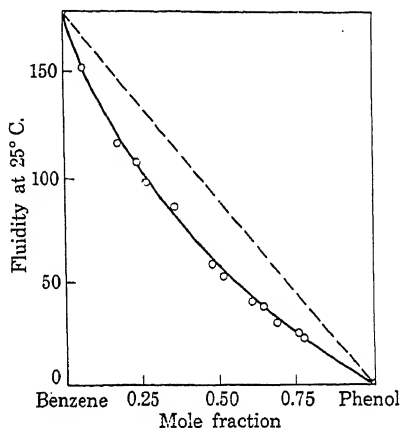


FIG. 125.—Observed and calculated fluidities of benzene-phenol mixtures. (Roseware, Powell and Eyring.)

* The negative sign is employed because diffusion occurs in the direction of decreasing concentration.

† It is not possible to say a priori whether these equilibrium positions refer to the solvent or solute; for large molecules or ions, they are probably those of the solvent (see page 520).

transported in each jump; the change of the standard free energy with distance can then be represented by the curve in Fig. 126. In the present discussion the assumption is made that the standard free energy is the same in the equilibrium positions that the molecule occupies in the course of diffusion; since the concentrations at the initial and final positions must be different, as otherwise diffusion would not occur, this condition can hold only if the solutions are ideal. The following treatment is

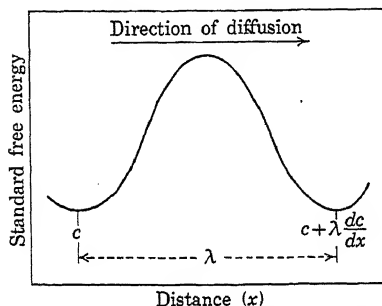


FIG. 126.—Free-energy barrier for diffusion in an ideal solution.

applicable, therefore, to ideal systems, or to solutions so dilute that they behave virtually in an ideal manner; the corrections to be made for departure from ideality will be considered later. It will be noted that if the standard free energy is the same in initial and final states and the energy barrier is assumed to be symmetrical, the free energy of

activation will be the same in the forward and backward directions; the specific rate constant k is, therefore, the same for flow in either direction.

The concentrations in moles per cubic centimeter of solute molecules in initial and final states of diffusion are c and $c + \lambda dc/dx$,* respectively, since dc/dx is the concentration gradient and λ is the distance between the successive equilibrium positions. The number of molecules moving in the forward direction, *i.e.*, from left to right, through a cross section of 1 sq. cm. is given by

$$v_f = Nc\lambda k \text{ molecules sq. cm.}^{-1} \text{ sec.}^{-1} \quad (100)$$

where N is, as before, the Avogadro number and k is the specific reaction rate for diffusion, *i.e.*, the number of times a molecule moves from one position to the next per second. Similarly, the rate of movement in the backward direction, *i.e.*, from right to left, is

$$v_b = N \left(c + \lambda \frac{dc}{dx} \right) \lambda k \text{ molecules sq. cm.}^{-1} \text{ sec.}^{-1} \quad (101)$$

* Since the concentration decreases in the direction of diffusion, dc/dx is negative and thus $c + \lambda(dc/dx)$ is less than c .

The resultant flow is from left to right and amounts to

$$v = -N\lambda^2k \frac{dc}{dx} \text{ molecules sq. cm.}^{-1} \text{ sec.}^{-1} \quad (102)$$

It will be seen from Eq. (99) that the resultant flow per square centimeter ($A = 1$) per second ($dt = 1$) can be expressed in terms of the diffusion coefficient as

$$v = -DN \frac{dc}{dx} \text{ molecules sq. cm.}^{-1} \text{ sec.}^{-1}, \quad (103)$$

the Avogadro number being introduced to change moles to molecules. It follows, therefore, that

$$DN \frac{dc}{dx} = N\lambda^2k \frac{dc}{dx}, \quad (104)$$

or

$$D = \lambda^2k. \quad (105)$$

As already mentioned, this equation can hold only for ideal solutions or dilute solutions that approximate to ideal behavior.

If λ and k for diffusion may be identified with the corresponding quantities for viscosity, as is particularly the case for self-diffusion, it is possible to introduce Eq. (21) with the result

$$D = \frac{\lambda_1 k T}{\lambda_2 \lambda_3 \eta}. \quad (106)$$

It is of interest to compare this with the classical equation (98); the latter contains $6\pi r$ in place of $\lambda_2 \lambda_3 / \lambda_1$ in the former, and although these quantities are of the same order of magnitude, *viz.*, 10^{-8} cm., the actual values may well differ by a factor of about 10. Strictly speaking, the two equations are not comparable, because the Stokes-Einstein equation is based on the assumption that the diffusing molecules are large and that the medium may be regarded as being continuous, the laws of classical hydrodynamics being applicable. In the deduction of Eq. (106), however, it has been supposed that the diffusing molecules and those of the medium have similar dimensions.

When a large molecule or ion diffuses or migrates electrically, in a solvent consisting of relatively small molecules, it is unlikely

that the rate-determining step will be the jump of the solute molecule from one equilibrium position to the next, since the work required to produce the necessary space would be very large. It is much more probable, therefore, that the jump of the solvent in one direction is the rate-determining process; the large molecule of solute then moves in the opposite direction into the space left vacant as a result of the motion of the solvent molecule. This conclusion is in agreement with the observation that the temperature coefficient of diffusion of large molecules and of the conductance of large ions is the same as the temperature coefficient of viscosity of the solvent. It is clearly the movement of the solvent molecules that determines the rate of diffusion of the solute in these instances. The manner in which

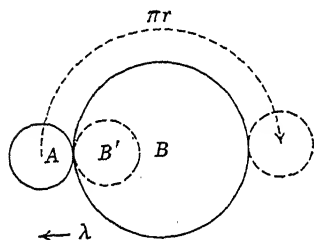


FIG. 127.—Diffusion of large molecule (B) due to movement of small solvent molecule (A).

this can occur is depicted diagrammatically in Fig. 127; the small solvent molecule A will move as shown by the arrow, in a series of jumps from one equilibrium position to another, until it has reached the position shown by the dotted circle. The large solute molecule B will then diffuse to the left to fill the space vacated by the solvent molecule. It is evident, therefore, that

the solvent molecule must move through a distance of at least πr , where r is the radius of the large diffusing molecule, in order that the latter may move from right to left a distance of approximately λ , where λ is the distance between successive equilibrium positions of the solvent molecule. If the solute molecule were small, however, *e.g.*, B', it would move from right to left a distance of approximately λ in each jump of the solvent molecule, and so it follows that

$$D_l = D_s \left(\frac{\lambda}{a\pi r} \right), \quad (107)$$

where D_l and D_s are the diffusion coefficients of large and small molecules in the same solvent and a is a factor of the order of unity which allows for the fact that the molecule A may not take the shortest path in its journey around B. The value of D_s is given by Eq. (106), which may be put in the form $D_s = kT/\lambda\eta$,

so that Eq. (107) becomes

$$D_i = \frac{kT}{a\pi r\eta} \quad (108)$$

According to the Stokes-Einstein equation (98) the factor a in Eq. (108) should be 6; but, as stated above, this involves the approximation of considering the solvent as a continuous medium. It appears probable, however, that in the diffusion of large molecules in a solvent consisting of small molecules a will not be greatly different from six.

Test of Diffusion Equations.—Since Eq. (106) should be exactly applicable to self-diffusion, it can best be tested by the data for the diffusion of heavy into light water.⁴⁷ From the measured viscosities and diffusion coefficients at 0 and 45°C. the quantity $\lambda_2\lambda_3/\lambda_1$ was found by Eq. (106) to be 1.43×10^{-7} cm. at 0°C. and 1.38×10^{-7} cm. at 45°C. Further, by assuming $\lambda_1\lambda_2\lambda_3$ to give the effective volume of a single molecule (*cf.* page 484), this quantity could be calculated from the molar volume. Combining the values for $\lambda_2\lambda_3/\lambda_1$ and $\lambda_1\lambda_2\lambda_3$ the following results were obtained:⁴⁸

	0°C.	45°C.
λ_1	1.44×10^{-8}	1.47×10^{-8} cm.
$(\lambda_2\lambda_3)^{1/2}$	4.54×10^{-8}	4.50×10^{-8} cm.

The fact that λ_1 is smaller than $(\lambda_2\lambda_3)^{1/2}$, and hence probably smaller than both λ_2 and λ_3 , is in agreement with the expectation that the plane of flow in diffusion will tend to coincide with the plane of the water molecule, since flow in this direction will take place most easily. Application of Eq. (98), based on Stokes's law, gives a value of r of 0.78×10^{-8} cm. at 0°C. and 0.73×10^{-8} cm. at 45°C.; these results are clearly too small for a molecule of water.

In the case of diffusion of a solute molecule through a solvent, it is not necessarily true that λ and k will be the same for viscous

⁴⁷ W. J. C. Orr and J. A. V. Butler, *J. Chem. Soc.*, 1273 (1935).

⁴⁸ Eyring, Ref. 1.

flow of the solvent as for diffusion,* and so Eq. (108) will not be strictly true. Nevertheless, even if the $\lambda^2 k$ terms in the expressions for D and η do not cancel, it is evident that the product $D\eta$ in different solvents will be related to the quantity $\lambda_1/\lambda_2\lambda_3$. It appears, therefore, that some relationship between $D\eta$ and the molar volume of the solvent would not be unexpected,⁴⁹ and it is of interest to record that in the diffusion of iodine, $D\eta$ increases with the molar volume when pairs of solvents of similar nature are compared; a few illustrations are recorded in Table LXIX.⁵⁰

TABLE LXIX.—RELATION BETWEEN $D\eta$ AT 19.9°C. IN VARIOUS SOLVENTS AND THEIR MOLAR VOLUMES

Solvents	Molar volume	$D\eta$
Dibromethane.....	87	1,232
Tetrabromethane.....	117	1,544
Chloroform.....	81	1,062
Carbon tetrachloride.....	97	1,128
Ethyl acetate.....	98	850
Isoamyl acetate.....	149	933

Temperature Coefficient of Diffusion.—The specific rate constant for diffusion is given, according to the theory of absolute reaction rates, by the expression

$$k = \frac{kT}{h} \cdot \frac{F_{\ddagger}}{F} e^{-\epsilon_0/kT}, \quad (109)$$

where F_{\ddagger} and F are the partition functions of the system in the activated and normal states, respectively, and ϵ_0 is the activation energy per molecule at 0°K. It is clear, therefore, that an

* The specific rate k for diffusion involves the free energy of activation of the rate-determining process, and this will probably be related to the mole fractions of both constituents and their respective $\Delta F_{\ddagger}^{\circ}$ values (cf. p. 515). It is only for very dilute solutions or for very large molecules, as implied above, that the free energy of activation for diffusion might be the value for the solvent and hence the same as that for the viscosity of the solvent. Under these conditions λ and k would be the same for viscosity and diffusion.

⁴⁹ Taylor, Ref. 46.

⁵⁰ C. C. Miller, *Proc. Roy. Soc.*, **103**, A, 724 (1924).

exponential variation of the coefficient of diffusion with temperature is to be expected, as is the case with viscosity.⁵¹ Further, as with diffusion, the unit process of flow requires the provision of additional space, although the hole that has to be made is not necessarily the full size of a molecule. The energy of activation for diffusion per mole ($E_{\text{diff.}}$) may thus be taken as a fraction $1/n$ of the energy of vaporization, as follows:

$$E_{\text{diff.}} = \frac{\Delta E_{\text{vap.}}}{n}. \quad (110)$$

An examination of the accurate data⁵² on the diffusion of tetrabromomethane in tetrachlor-ethane shows that the exponential relationship holds accurately, the activation energy being 3,490 cal. The variation of the viscosity of tetrachlorethane with the temperature gives an activation energy of 2,995 cal. for viscous flow, a value that is almost exactly one-third of the molecular heat of vaporization of this substance. The data for tetrabromomethane are not available; but, upon assuming the same Trouton constant as for tetrachlor-ethane, the heat of vaporization is estimated as 11,230 cal., and hence the activation energy for viscosity should be one-third of this value, *viz.*, 3,745 cal. It is of interest to note that the mean of the values for the two halogenoethanes, *viz.*, 3,370 cal., is almost exactly equal to the activation energy for diffusion; it appears, therefore, that in the process of diffusion the motion of one molecule past the other demands a free energy lying between those required by the two molecules in their separate viscous flows.

It has been seen (page 505) that the activation energy for the viscous flow of water diminishes with increasing temperature, a fact that has been explained on the basis of the hydrogen-bond structure of the liquid; an analogous behavior is clearly to be expected for a solute diffusing in an aqueous solution. The results for the diffusion of mannitol in water⁵³ are in harmony with expectation; the activation energy falls from 6,600 cal. between 0 and 10°C. to 3,800 cal. between 60 and 70°C. These values

⁵¹ Cf. H. Braune, *Z. physik. Chem.*, **110**, 147 (1924); R. S. Bradley, *J. Chem. Soc.*, 1910 (1934); E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 1225 (1937).

⁵² E. Cohen and H. R. Bruins, *Z. physik. Chem.*, **103**, 404 (1923).

⁵³ J. D. R. Scheffer and F. E. C. Scheffer, *Proc. Acad. Sci. Amsterdam*, **19**, 148 (1916).

are approximately 1 kcal. larger than the corresponding activation energies for viscous flow; this difference can be readily understood in view of the large size of the mannitol molecule and the fact that it has a greater capacity than a water molecule for forming hydrogen bonds. The data for the coefficients of diffusion in aqueous solutions at several temperatures are limited, but the results in general lead to activation energies for diffusion in satisfactory agreement with those for the viscosity of water in the same temperature range.⁵⁴

It has been observed that solutes possessing large diffusion coefficients invariably have small temperature coefficients;⁵⁵ it is evident from (105) and (109) that the diffusion coefficient may be expressed by

$$D = \lambda^2 \frac{kT}{h} \cdot \frac{F_{\ddagger}}{F} e^{-\epsilon_0/kT}, \quad (111)$$

so that, in general, a high value of D implies a small activation energy and hence a small temperature coefficient, as found in practice. The same inverse relationship between the diffusion coefficient and its temperature coefficient has been observed in connection with the diffusion of bromoform and iodine in various media. Qualitatively, the significance of this fact is that the more slowly diffusing substances have to form relatively large holes for the activated state; the activation energy and hence the temperature coefficient of diffusion are consequently large.⁵⁶

Since $(F_{\ddagger}/F) e^{-\epsilon_0/kT}$ is equal to K^{\ddagger} , in the usual manner (page 188), it is possible to write Eq. (111) as

$$D = \lambda^2 \frac{kT}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}; \quad (112)$$

and since diffusion is accompanied by a negligible volume change, it follows (cf. page 198) that

$$D = e\lambda^2 \frac{kT}{h} e^{\Delta S^{\ddagger}/R} e^{-E/RT}, \quad (113)$$

where E is the observed activation energy for diffusion derived from the equation $D = A e^{-E/RT}$. Since A and E can be obtained

⁵⁴ Taylor, Ref. 46.

⁵⁵ W. Öholm, *Z. physik. Chem.*, **50**, 309 (1904); **70**, 378 (1910); *Meddel. Vetenskapsakad. Nobelinst.*, **2**, [23, 24, 26] (1912).

⁵⁶ Taylor, Ref. 46.

from experimental determinations of the diffusion coefficient at two or more temperatures, it is possible, by means of Eq. (113), to calculate $\lambda^2 e^{\Delta S^\ddagger/R}$ or its square root. Some results obtained in this manner are quoted in Table LXX.⁵⁷ With the exception

TABLE LXX.—ENTROPY FACTOR FOR DIFFUSION

Diffusion system	$A \times 10^3$, cm. ² sec. ⁻¹	E , kcal.	$\lambda(e^{\Delta S^\ddagger/R})^{1/2}$, Å
Water in water.....	197	5.30	11.0
Phenol in methyl alcohol.....	3.4	3.15	1.4
Phenol in benzene.....	3.16	3.08	1.4
Tetrabrom- in tetrachlor-ethane.....	1.68	1.68	1.0
Bromine in carbon disulfide.....	0.43	15.36	0.4

of the value of $\lambda(e^{\Delta S^\ddagger/R})^{1/2}$ for the self-diffusion of water, the results in the last column indicate that ΔS^\ddagger cannot differ appreciably from zero; *i.e.*, $e^{\Delta S^\ddagger/R}$ is approximately unity, and the figures given are roughly equal to λ , the distance from one equilibrium position to the next in diffusion. The high result for water, which is greatly in excess of the value to be expected for λ (*cf.* page 521), means that the formation of the activated state for diffusion of a water molecule is accompanied by an appreciable increase of entropy. This is as anticipated and is in harmony with the conclusions reached from a consideration of the viscosity of water (page 506).

Absolute Values of Diffusion Rates.⁵⁸—The absolute magnitudes of diffusion coefficients can be determined by evaluating the partition functions in Eq. (111); if the degree of freedom corresponding to the diffusional movement is assumed to be a translational one, as in the case of viscosity, the ratio of the partition functions F_\ddagger/F will be of the form given by Eq. (31). Upon writing $E_{\text{diff.}}/RT$ in place of ϵ_0/kT and replacing $E_{\text{diff.}}$ by $\Delta E_{\text{vap.}}/n$, as previously explained, Eq. (111) becomes

$$D = \lambda^2 \frac{kT}{h} \cdot \frac{h}{(2\pi mkT)^{1/2} v_f^{1/2}} e^{-\Delta E_{\text{vap.}}/nRT} \quad (114)$$

$$= \frac{\lambda^2}{v_f^{1/2}} \left(\frac{kT}{2\pi m} \right)^{1/2} e^{-\Delta E_{\text{vap.}}/nRT}. \quad (115)$$

⁵⁷ R. M. Barrer, *Trans. Faraday Soc.*, **35**, 644 (1939).

⁵⁸ A. E. Stearn, E. M. Irish and H. Eyring, *J. Phys. Chem.*, **44**, 981 (1940).

The distance λ may be taken as approximately $(V/N)^{1/3}$, where V is the molar volume, and the free volume may be estimated by one of the methods described on page 478; hence, it should be possible to evaluate the diffusion coefficient provided that $\Delta E_{\text{vap.}}$ is known, n being taken as 3. It must be remembered, however, that in general diffusion involves molecules of two types, *viz.*, solvent and solute; hence, mean values of λ , $v_f^{1/3}$ and $\Delta E_{\text{vap.}}$ might reasonably be employed. For λ and $v_f^{1/3}$, weighed arithmetic means of the values for the two pure components are obtained from the expressions

$$\lambda = N_1\lambda_1 + N_2\lambda_2 \quad (116)$$

and

$$v_f^{1/3} = N_1v_{f_1}^{1/3} + N_2v_{f_2}^{1/3} \quad (117)$$

where N_1 and N_2 are the mole fractions of the substances indicated by the subscripts; the mean value of $\Delta E_{\text{vap.}}$ was calculated from the equation

$$\Delta E_{\text{vap.}}^{1/2} = N_1 \Delta E_1^{1/2} + N_2 \Delta E_2^{1/2}. \quad (118)$$

The mass m employed in Eq. (115) was taken as the reduced mass of the two constituent molecules treated as a combined unit.* The results quoted in Table LXXI were obtained in the

TABLE LXXI.—CALCULATION OF DIFFUSION COEFFICIENTS OF TETRABROM-INTO TETRACHLOR-ETHANE

Temp., °K.	$\lambda^2 \times 10^{15}$	$v_f^{1/3} \times 10^9$	E , kcal.	$D \times 10^5 \text{ cm.}^2 \text{ sec.}^{-1}$	
				Calc.	Obs.
273.4	3.12	6.45	9.85	0.64	0.35
288.0	3.15	6.92	9.72	0.92	0.50
308.6	3.19	7.59	9.52	1.42	0.74
324.1	3.23	8.13	9.38	1.89	0.95

manner described for the diffusion of tetrabromomethane into the corresponding chloro-compound. Comparison of the figures in the last two columns of the table shows that, although the calculated diffusion coefficient is of the correct order of mag-

* This implies that the unit of flow involves one molecule of solute and one of solvent, which is probably not correct (*cf.* p. 534), but the error is small.

nitude, it is about twice the observed value. A discrepancy of this nature is frequently to be found with organic liquids; it may be due to the approximation employed, in evaluating the ratio of the partition functions, of taking the rotational and vibrational contributions to be the same in the normal and activated states. For a structureless liquid, it is likely that there will be more freedom of rotation in the initial than in the activated states; the ratio of the rotational contributions to F_{\ddagger}/F involved in Eq. (111) will thus not be unity, but somewhat less. The effect of taking rotation into consideration would thus be to reduce the calculated diffusion coefficients to some extent. It will be seen later that where the solvent has structure, as in the case of water, the rotational contributions should operate in the opposite sense and make the diffusion coefficients calculated by Eq. (115) too small.

When the solutions are dilute, the values of λ , v_f and ΔE_{vap} may be taken as those of the pure solvent; this has been done in calculating the diffusion coefficients of various solutes in benzene. Some of the results obtained, n being taken as 3, are given in Table LXXII.

TABLE LXXII.—CALCULATION OF DIFFUSION COEFFICIENTS IN BENZENE AT 280.5°K.

Solute	$D \times 10^5 \text{ cm.}^2 \text{ sec.}^{-1}$	
	Calc.	Obs.
Carbon tetrachloride.....	3.40	1.51
Iodoform.....	3.04	1.12
Methyl iodide.....	3.46	2.06
n-Amyl iodide.....	3.28	1.41
Ethylene chloride.....	3.71	1.77
Brombenzene.....	3.39	1.45
1:2:4-Trichlorbenzene.....	3.33	1.34
Naphthalene.....	3.52	1.19

In Table LXXIII are recorded the results for the diffusion of brombenzene, bromoform and iodine in various solvents; the value of n found to hold for viscous flow was used as far as possible, such values being marked by an asterisk. In other cases, n has been assigned by analogy with chemically similar substances for which the values are known. It is seen, as before,

that although the discrepancy between the calculated and experimental diffusion coefficients is not great, the former are always somewhat larger than the latter.

TABLE LXXIII.—CALCULATION OF DIFFUSION COEFFICIENTS

Solvent	n	$D \times 10^5 \text{ cm.}^2 \text{ sec.}^{-1}$	
		Calc.	Obs.
Diffusion of brombenzene (280.5°K.):			
Ether.....	4*	16.5	3.50
Hexane.....	4*	13.3	2.49
Cyclohexane.....	3*	3.34	1.16
Toluene.....	4*	7.4	1.59
<i>m</i> -Xylene.....	4	4.9	1.52
Diffusion of bromoform (293°K.):			
Acetone.....	4*	12.0	2.69
Ether.....	4*	17.3	3.39
Benzene.....	3*	3.7	1.69
Methyl alcohol.....	3	2.64	1.93
Amyl alcohol.....	3	0.94	0.52
Diffusion of iodine (293°K.):			
Chloroform.....	4*	10.1	2.12
Ethyl acetate.....	4*	9.8	2.15
Carbon disulfide.....	4*	12.4	3.12
Heptane.....	4*	11.4	2.77
Benzene.....	3*	3.79	1.93
Brombenzene.....	3	1.71	1.20

Diffusion in Aqueous Solutions.⁵⁹—The most complete data on diffusion in water are those for mannitol, and these may be compared with the results derived from Eq. (115). For the purpose of the calculations, n was taken as 2.4 throughout, and a mean value of 9,700 was employed for $\Delta E_{\text{vap.}}$. Since the two methods for obtaining free volumes described at the beginning of this chapter give different values for water, both have been employed in obtaining the results given in Table LXXIV. It is seen that better values for the diffusion coefficient of mannitol in water are obtained by using Eq. (9) to obtain the free volume, but in any case the calculated values are now always less than those found by experiment. Since water has a structure, and it appears from the viscosity studies (page 505) that

⁵⁹ Stearn, Irish and Eyring, Ref. 58.

the hydrogen bonds are broken to a considerable extent in the formation of the activated state, it is apparent that there will be more freedom of movement in the activated than in the initial

TABLE LXXIV.—DIFFUSION OF MANNITOL IN WATER

Temp., °K.	$D \times 10^5 \text{ cm.}^2 \text{ sec.}^{-1}$		
	Calc.		Obs.
	v_f from Eq. (12)	v_f from Eq. (9)	
273.0	0.096	0.26	0.26
296.2	0.18	0.43	0.61
316.4	0.29	0.63	0.97
335.0	0.42	0.89	1.35
343.2	0.50	1.05	1.56

state. As seen above the inclusion of the rotational contribution to the partition function would, in these circumstances, lead to diffusion coefficients larger than those given by Eq. (115) which was used to derive the results in Table LXXIV.

TABLE LXXV.—DIFFUSION COEFFICIENTS IN WATER

Solute	Temp., °K.	$D \times 10^5 \text{ cm.}^2 \text{ sec.}^{-1}$	
		Calc.	Obs.
Methy. alcohol.....	291	0.39	1.37
Amyl alcohol.....	291	0.34	0.88
Phenol.....	291	0.34	0.80
Glycerol.....	293	0.36	0.83
Pyrogallol.....	291	0.33	0.61
Urea.....	293	0.38	1.18
Caffein.....	293	0.34	0.57
Urethane.....	291	0.38	0.87
Glucose.....	291	0.32	0.57
Sucrose.....	293	0.34	0.57
Various dyes.....	291	~0.3	0.17 to 0.58
Various proteins.....	280-290	~0.3	0.04 to 0.13

Some miscellaneous data for diffusion in water are collected in Table LXXV; the free volume calculated by means of Eq. (9), which gave the best results in connection with mannitol (Table

LXXIV), has been used throughout. The observed diffusion coefficients are those recorded for the most dilute solutions that have been studied. Calculations have also been made for the rates of diffusion of the gases acetylene, carbon dioxide, nitrogen and hydrogen in water; the values are in each case approximately four times those found by experiment.

Diffusion in Concentrated (Nonideal) Solutions.⁶⁰—As explained on page 518, the equations developed so far have neglected any deviation from ideal behavior, and this approximation is probably justified in the cases considered hitherto. The fact that activity, and not concentration, is the driving force in

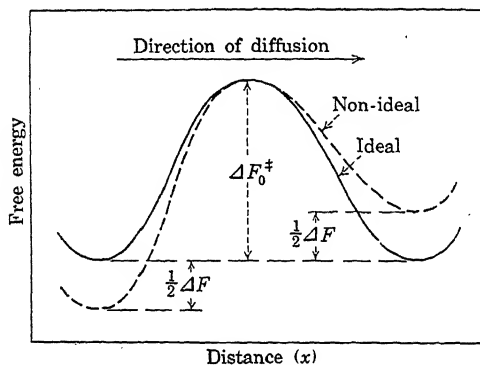


FIG. 128.—Free-energy barrier for diffusion in ideal and nonideal systems.

diffusion is brought out clearly by consideration of a system forming two layers, liquid or solid, in equilibrium. In spite of the marked differences in concentration that generally exist, there is no diffusion across the boundary. It is clear, therefore, that the cause of diffusion is the difference in free energy between different parts of the system. For systems that depart appreciably from ideality, so that the standard free energies are different in initial and activated states, a modified treatment must be adopted. One procedure is to calculate the total free energy arising from nonideal behavior; then, since the energy barrier is symmetrical, one-half of this quantity will contribute to the free energy of the activation process in each direction. The variation of the free energy between initial and final states in the act of diffusion is shown in Fig. 128; ΔF represents the free-energy change arising from nonideality. If $d \ln \gamma_1/dx$ represents

⁶⁰ Stearn, Irish and Eyring, Ref. 58.

the rate of change of $\ln \gamma_1$, where γ_1 is the activity coefficient of the compound 1, with distance x in the direction of diffusion, then the change in $\ln \gamma_1$ between initial and final states in the elementary act of diffusion is $\lambda(d \ln \gamma_1/dx)$; it follows, therefore, that the corresponding change in free energy is

$$\Delta F = \lambda RT \frac{d \ln \gamma_1}{dx} \quad (119)$$

$$= \lambda RT \frac{d \ln \gamma_1}{dN_1} \cdot \frac{dN_1}{dx} \quad (120)$$

$$= \lambda \frac{dN_1}{dx} G_1, \quad (121)$$

where N_1 is the mole fraction and G_1 is defined by

$$G_1 \equiv RT \frac{d \ln \gamma_1}{dN_1}. \quad (122)$$

If ΔF_0^\ddagger is the free energy of activation in each direction for an ideal system, then, when the solution is not ideal,

$$\Delta F_f^\ddagger = \Delta F_0^\ddagger + \frac{1}{2} \Delta F \quad (123)$$

$$= \Delta F_0^\ddagger + \frac{1}{2} \lambda \frac{dN_1}{dx} G_1, \quad (124)$$

ΔF_f^\ddagger being the free energy of activation for the forward direction. Similarly, ΔF_b^\ddagger for the backward direction is given by

$$\Delta F_b^\ddagger = \Delta F_0^\ddagger - \frac{1}{2} \lambda \frac{dN_1}{dx} G_1. \quad (125)$$

The net rate v of diffusion of constituent 1 from left to right is then a modified form of Eq. (102), *viz.*,

$$v = N c_1 \lambda k_f - N \left(c_1 + \lambda \frac{dc_1}{dx} \right) \lambda k_b \text{ molecules sq. cm.}^{-1} \text{ sec.}^{-1}, \quad (126)$$

where k_f and k_b are the specific rates for diffusion in the forward and backward directions. According to the theory of absolute reaction rates, these may be defined in terms of ΔF_f^\ddagger and ΔF_b^\ddagger , thus:

$$k_f = \frac{kT}{h} e^{-\Delta F_f^\ddagger/RT} \quad (127)$$

and

$$k_b = \frac{kT}{h} e^{-\Delta F_b^\ddagger/RT}. \quad (128)$$

Upon introducing the value of ΔF_f^\ddagger given by Eq. (124), k_f becomes

$$k_f = \frac{kT}{h} e^{-\Delta F_0^\ddagger/RT} e^{-\frac{1}{2}\lambda \frac{dN_1}{dx} \cdot \frac{G_1}{RT}} \quad (129)$$

$$= \frac{kT}{h} e^{-\Delta F_0^\ddagger/RT} e^{-\alpha}, \quad (129a)$$

where α is written for $\frac{1}{2}\lambda \frac{dN_1}{dx} \cdot \frac{G_1}{RT}$ to simplify the representation.

The specific rate for either forward or backward direction for an ideal system, which has previously been given the symbol k , is defined by

$$k = \frac{kT}{h} e^{-\Delta F_0^\ddagger/RT}, \quad (130)$$

and so Eq. (129a) may be written

$$k_f = k e^{-\alpha}. \quad (131)$$

Similarly, the analogous expression for k_b is

$$k_b = k e^{\alpha}. \quad (132)$$

If these values for k_f and k_b are now substituted in Eq. (126), the result is

$$v = Nc_1\lambda k(e^{-\alpha} - e^{\alpha}) - N\lambda^2k \frac{dc_1}{dx} e^{\alpha} \text{ molecules sq. cm.}^{-1} \text{ sec.}^{-1} \quad (133)$$

Since $2RT \gg \lambda(dN_1/dx)G_1$, the quantity α is much less than unity; the exponentials may thus be expanded and all terms beyond the first neglected. Hence,

$$v = -Nc_1\lambda k(2\alpha) - N\lambda^2k \frac{dc_1}{dx} (1 + \alpha) \quad (134)$$

$$= -Nc_1\lambda k(2\alpha) - N\lambda^2k \frac{dc_1}{dx}, \quad (135)$$

if α is neglected in comparison with unity in the extreme right-

hand term of Eq. (134). Upon inserting the value of α , Eq. (135) becomes

$$v = -Nc_1\lambda^2k \frac{dN_1}{dx} \cdot \frac{G_1}{RT} - N\lambda^2k \frac{dc_1}{dx}. \quad (136)$$

Writing $N_1(d c_1/dx)$ in place of $c_1(dN_1/dx)$ in the first term on the right-hand side,* it follows that

$$v = -N\lambda^2k \frac{dc_1}{dx} \left(\frac{N_1 G_1}{RT} + 1 \right). \quad (137)$$

As seen on page 519, the rate of diffusion can also be represented by

$$v = -D_1 N \frac{dc_1}{dx}; \quad (138)$$

hence, it follows that

$$D_1 = \lambda^2k \left(\frac{N_1 G_1}{RT} + 1 \right). \quad (139)$$

According to Eq. (105), λ^2k is equal to the coefficient of diffusion in an ideal system; if this quantity is represented by D_1^0 and the value of G_1 is introduced from (122), Eq. (139) becomes

$$D_1 = D_1^0 \left(1 + N_1 \frac{d \ln \gamma_1}{d N_1} \right) \quad (140)$$

$$= D_1^0 \left(1 + \frac{d \ln \gamma_1}{d \ln N_1} \right) \quad (141)$$

$$= D_1^0 \frac{d \ln a_1}{d \ln N_1}, \quad (142)$$

where the activity a_1 is equal to $N_1 \gamma_1$. Equations (140) to (142) are identical in form with that derived by L. Onsager and R. M. Fuoss for dilute solutions of electrolytes.⁶¹

Attention should be called to the fact that the foregoing deductions are based on the assumption that one molecule only is involved in the rate-determining stage of the diffusion process; if a molecule of each constituent had been involved, ΔF in Eq.

* Strictly speaking, a small correction factor should be included in changing from concentrations to mole fractions, but this will be absorbed in λ^2 .

⁶¹ L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2687 (1932); see also A. R. Gordon *et al.*, *J. Chem. Phys.*, **5**, 522 (1937); **7**, 89, 963 (1939); P. van Rysselberghe, *J. Am. Chem. Soc.*, **60**, 2326 (1938).

(119) would have included a similar term, with a negative sign for the change with distance of the activity coefficient of the second component. In view of the agreement with experiment obtained by means of Eq. (142), as described below, it seems probable that one molecule only is concerned in each activated jump in diffusion. This should not be taken to imply that all the jumping is done by one molecular species; actually both types of molecules must take part in the process, although each elementary rate-determining act involves only one or the other and not both.

An alternative method⁶² of deriving Eq. (142), which is the same in principle as that already given but is somewhat simpler to carry through, is based on the use of the general equation (4), Chap. VIII, for nonideal systems. For the present purpose the specific rate for diffusion may be written as

$$k = \frac{kT}{h} K^\ddagger \frac{\gamma}{\gamma_\ddagger} = k_0 \frac{\gamma}{\gamma_\ddagger}, \quad (143)$$

where k_0 is the specific rate in an ideal system, γ is the activity coefficient of the diffusing molecule in its initial state and γ_\ddagger that in the activated state. If γ_1 is the activity coefficient of component 1 in its initial state, then in the final state, after having jumped through a distance λ , its activity coefficient will be $\gamma_1 + \lambda d\gamma_1/dx$; further, if, as assumed above, the energy barrier is symmetrical,* the activity coefficient in the activated state will be $\gamma_1 + \frac{1}{2}\lambda d\gamma_1/dx$. It follows, therefore, that v_f , the rate in the forward direction, is

$$v_f = Nc_1\lambda k_0 \frac{\gamma_1}{\gamma_1 + \frac{\lambda}{2} \cdot \frac{d\gamma_1}{dx}} \quad (144)$$

and the rate v_b in the backward direction is

$$v_b = N \left(c_1 + \lambda \frac{dc_1}{dx} \right) \lambda k_0 \frac{\gamma_1 + \lambda \frac{d\gamma_1}{dx}}{\gamma_1 + \frac{\lambda}{2} \cdot \frac{d\gamma_1}{dx}} \quad (145)$$

⁶² Powell, Roseveare and Eyring, Ref. 17.

* The final result obtained, as in the previous treatment, is independent of the shape of the barrier; a symmetrical barrier is assumed for convenience.

Since λ is small, the fractions involving γ may be simplified, thus:

$$\frac{\gamma_1}{\gamma_1 + \frac{\lambda}{2} \cdot \frac{d\gamma_1}{dx}} \approx 1 - \frac{\lambda}{2} \cdot \frac{d \ln \gamma_1}{dx} \quad (146)$$

and

$$\frac{\gamma_1 + \lambda \frac{d\gamma_1}{dx}}{\gamma_1 + \frac{\lambda}{2} \cdot \frac{d\gamma_1}{dx}} \approx 1 + \frac{\lambda}{2} \cdot \frac{d \ln \gamma_1}{dx}. \quad (147)$$

The net rate of diffusion v , which is obtained by subtracting the backward from the forward rate, is then given by

$$v = Nc_1\lambda k_0 \left(1 - \frac{\lambda}{2} \cdot \frac{d \ln \gamma_1}{dx} \right) - N \left(c_1 + \lambda \frac{dc_1}{dx} \right) \lambda k_0 \left(1 + \frac{\lambda}{2} \cdot \frac{d \ln \gamma_1}{dx} \right). \quad (148)$$

If the term involving λ^3 is neglected, as it will be very small, this equation reduces to

$$v = -Nc_1\lambda^2 k_0 \frac{d \ln \gamma_1}{dx} - N\lambda^2 k_0 \frac{dc_1}{dx} \quad (149)$$

$$= -N\lambda^2 k_0 \frac{dc_1}{dx} \left(c_1 \frac{d \ln \gamma_1}{dc_1} + 1 \right). \quad (150)$$

As before, the units in the parentheses may be changed from concentrations to mole fractions, so that

$$v = -N\lambda^2 k_0 \frac{dc_1}{dx} \left(N_1 \frac{d \ln \gamma_1}{dN_1} + 1 \right), \quad (151)$$

which is identical with Eq. (137) and so leads to the same final result.

Test of Diffusion Equations for Nonideal Systems.⁶³—A convenient method of testing Eq. (142) is to multiply both sides by η , the viscosity of the system, thus,

$$D_{1\eta} = D_{1\eta}^0 \left(\frac{d \ln a_1}{d \ln N_1} \right), \quad (152)$$

⁶³ Powell, Roseveare and Evring, Ref. 17.

and to replace $D_1^0\eta$ by its equivalent, as given by Eq. (106), for an ideal system; it follows, therefore, that

$$D_1\eta = \frac{\lambda_1 kT}{\lambda_2 \lambda_3} \cdot \frac{d \ln a_1}{d \ln N_1} \quad (153)$$

The activity of the component 1 is proportional to its partial vapor pressure p_1 in the mixture, and so Eq. (153) can be written

$$D_1\eta / \frac{d \ln p_1}{d \ln N_1} = \frac{\lambda_1}{\lambda_2 \lambda_3} kT. \quad (154)$$

The values of $\lambda_1\lambda_2$ and λ_3 are mean values for the constituents of the mixture; and if they are taken to be a linear function of

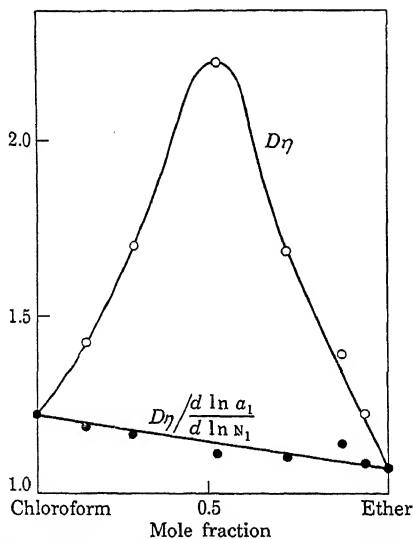


FIG. 129.—Variation of D_η with concentration in the chloroform-ether system. (Roseveare, Powell and Eyring.)

the mole fraction (cf. page 526), it follows that the plot of the left-hand side of Eq. (154) against the mole fraction should be a straight line. This has been confirmed in a number of instances for which vapor-pressure data are available; one of the most striking cases is the ethyl ether-chloroform system, the results for which are shown in Fig. 129. Alternative methods of testing Eq. (154) are to assume the linear relationship and either to calculate $D_1\eta$ from vapor-pressure data or to derive the vapor

pressure of the constituent 1 from the values of $D_{1\eta}$ over the range of concentrations.

Diffusion in Solids.⁶⁴—Although diffusion in solids is fundamentally similar to diffusion in liquids, certain complications arise in the former case; these are due to the existence in solids of rifts arising from mechanical defects and of interfaces between grain boundaries through which diffusion can sometimes occur. Diffusion in a solid may, therefore, take place either as "volume diffusion," *i.e.*, homogeneously through the crystal lattice, or as "grain boundary diffusion," or "interface diffusion," which may occur along rifts at the interface between the grain and the surrounding material or at the interface of the crystal. The importance of distinguishing between these types of diffusion lies in the fact that they will occur at very different rates; consideration of the rates and activation energies of diffusion can sometimes be employed to identify the type.

The theory of absolute reaction rates may be applied to diffusion in a solid in the same way as it has been to liquid diffusion (page 518), and the same equation $D = \lambda^2 k$ derived; the specific rate constant k is given by an equation of the form of (105), and therefore [cf. Eq. (111)]

$$D = \lambda^2 \frac{kT}{h} \cdot \frac{F_{\ddagger}}{F} e^{-\epsilon_0/kT}. \quad (155)$$

If, as before, the movement over the barrier is assumed to be equivalent to a translational degree of freedom, Eq. (155) may be written in a manner analogous to (115); this is equivalent to the expression

$$D = aT^{1/2} e^{-E/RT}, \quad (156)$$

which is similar to the equation proposed by O. W. Richardson for the diffusion of hydrogen through platinum.⁶⁵ On the other hand, if the degree of freedom corresponding to the diffusional movement in the solid phase is regarded as a vibration, there will be one degree of vibrational freedom more in the initial than in the activated state, so that Eq. (155) can be written as

$$D = \lambda^2 \frac{kT}{h} (1 - e^{-h\nu/kT}) e^{-\epsilon_0/kT}. \quad (157)$$

⁶⁴ A. E. Stearn and H. Eyring, *J. Phys. Chem.*, **44**, 955 (1940).

⁶⁵ O. W. Richardson, J. Nicol and T. Parnell, *Phil. Mag.*, **8**, 1 (1904).

If the frequency ν of the atoms in the solid is small, so that $h\nu \ll kT$, expansion of the exponential, only the term involving the first power of the exponent being retained, gives

$$D = \lambda^2 \nu e^{-E/RT}, \quad (158)$$

which is of the form of the equations of I. Langmuir and S. Dushman⁶⁶ and of J. A. M. van Liempt.⁶⁷

Diffusion of Metals through Metals.⁶⁸—For the purpose of studying the diffusion of one metal in another, Eq. (157) may be employed; λ is taken as $(V/N)^{1/4}$, where V is the gram-atomic volume and N is the Avogadro number; ν is taken as the average vibration frequency of the atoms in the lattice, and this is three-fourths of the Debye limiting frequency. It follows, therefore, that

$$D = \left(\frac{V}{N}\right)^{3/4} \cdot \frac{kT}{h} (1 - e^{-3\theta/4T}) e^{-\epsilon_0/kT} \quad (159)$$

$$= A e^{-E/RT}, \quad (160)$$

where θ is the Debye characteristic temperature. By use of the appropriate values of V and θ for a number of metals the magnitude of A in Eq. (160) was calculated to lie in the range of 0.0013 to 0.0042. From experimental diffusion data, however, the quantity A is found to have values of 10^{-5} to 10, and hence it appears that there has been an over-simplification in writing Eq. (159), the effect of the atoms other than those which are passing each other having been neglected.

Two other models of the diffusion process may be considered: (1) the diffusion of individual atoms into empty lattice positions, and (2) the rotation past each other of a pair of atoms, the additional free volume in the activated state being provided by compression of the neighboring atoms. The first of the processes would require an activation energy of the same order as the energy of sublimation,* since this energy is required to make a hole the size of an atom. The observed activation energies

⁶⁶ I. Langmuir and S. Dushman, *Phys. Rev.*, **20**, 113 (1922).

⁶⁷ J. A. M. van Liempt, *Z. anorg. Chem.*, **195**, 356 (1931); *Rec. trav. chim.*, **51**, 114 (1932).

⁶⁸ Stearn and Eyring, Ref. 64.

* This is based on the assumption that the energy of the crystal is mainly the sum of the binding energies of pairs of atoms.

are, however, about one-half to one-third of the expected magnitude for this mechanism of diffusion. On the second model the lattice must be slightly deformed in order to permit rotation of a pair of atoms; the free energy ΔF necessary to make a hole of sufficient size is given in terms of the compressibility by

$$\Delta F = \int_0^V \frac{1}{\beta} dV, \quad (161)$$

where β is taken as one-half the arithmetic mean of the compressibilities of the two molecules passing each other plus one-half the compressibility of the surrounding molecules and V is the arithmetic mean of the volumes of the two atoms passing each other. It is clear, however, that Eq. (161) will give a value which is higher than the free energy of activation of the process, since a fraction only of the mean atomic volume is adequate to permit rotation to take place; this fraction may be represented by $1/\alpha$, so that

$$\frac{\Delta F}{\Delta F^\ddagger} = \alpha, \quad (162)$$

where ΔF is given by Eq. (161) and ΔF^\ddagger is obtained from the data by means of the equation

$$D = \lambda^2 \frac{kT}{h} e^{-\Delta F^\ddagger/RT} \quad (163)$$

based on the relationship $D = \lambda^2 k$ and the value of k from the theory of absolute reaction rates [cf. Eq. (130)]. A selection of the results obtained in this manner, together with the corresponding activation energies $E_{\text{act.}}$, is given in Table LXXVI.

It is seen that the value of α generally lies between 5 and 10, the average for a large number of cases being 7.6; this can be interpreted to mean that on the average a hole about one-eighth of the mean atomic volume is sufficient to permit diffusion past each other of a pair of atoms. It will also be observed that α for self-diffusion of a given metal is, on the whole, smaller than for the diffusion into it of another metal; this can be explained by the fact that the more nearly perfect the lattice, *i.e.*, the purer the metal, the larger the free energy required to pass to the comparatively disordered activated state. In accordance with this view, it has been found that in the case of diffusion in

alloys the value of α increases, *i.e.*, ΔF^\ddagger decreases, with increasing concentration of the alloy.

TABLE LXXVI.—DIFFUSION OF METALS IN METALS

Diffusing metal	Temp., °K.	$E_{\text{act.}}$, kcal.	ΔF^\ddagger , kcal.	α
Diffusion into copper:				
Zinc.....	1000	19.7	36.0	5.8
Palladium.....	1000	21.9	39.5	7.1
Gold.....	1000	22.5	37.2	8.2
Nickel.....	1000	29.8	40.0	6.1
Tin.....	1000	31.2	33.2	8.4
Diffusion into lead:				
Silver.....	558	15.2	13.0	13.5
Cadmium.....	558	15.4	16.4	10.2
Bismuth.....	558	18.6	19.0	10.3
Tin.....	558	24.0	20.0	9.5
Mercury.....	460	19.0	15.6	9.7
Diffusion into gold:				
Copper.....	1000	27.4	33.8	10.7
Palladium.....	1000	37.4	42.5	10.2
Platinum.....	1000	39.0	43.9	10.7
Self-diffusion:				
Lead.....	558	28.0	21.0	9.3
Gold.....	1000	51.0	46.4	10.0
Copper.....	1000	57.2	43.5	5.4

The activation energies in Table LXXVI are, on the average, one-half to one-third the sublimation energies of the solute metals; this result may be compared with the ratio of the vaporization energy of a liquid metal to the activation energy for viscosity which is in the range of 9 to 20 (page 496). The interlocking of the atoms in their lattices in the solid state makes the formation of the hole more difficult than in the liquid.

Surface Diffusion.⁶⁹—Measurements have been made of the diffusion of thorium through tungsten, as well as into grain boundaries and on the surface, and the results are of interest; these are recorded in Table LXXVII, ΔF^\ddagger being obtained with the aid of Eq. (163), ΔH^\ddagger from the temperature coefficient, in the usual manner (*cf.* page 522) and ΔS^\ddagger from the thermodynamic relationship between the three quantities. It is to be expected

⁶⁹ I. Langmuir, *J. Franklin Inst.*, **217**, 543 (1934).

that for surface diffusion the formation of the activated state will involve the breaking of about one-half as many bonds as for the solid solution type of diffusion; it should be noted, therefore, that ΔH^\ddagger in the former case (62.4 kcal.) is approximately one-half that for the latter (116.0 kcal.). Since the entropies are small in both instances, the free energies of activation are seen to be in roughly the same proportion as the heats of activation.

TABLE LXXVII.—DIFFUSION OF THORIUM INTO AND ON TUNGSTEN

Types of diffusion	ΔF^\ddagger , kcal.	ΔH^\ddagger , kcal.	ΔS^\ddagger , e.u.
Solid solution.....	105.7	116.0	5.18
Grain boundary.....	76.9	86.0	4.58
Surface.....	55.1	62.4	3.68

Effect of Pressure on Solid Diffusion.—Though very little is known of the effect of pressure on diffusion in solids, important information regarding the mechanism of diffusion could be obtained from such data. Two models, which probably correspond to those already discussed, may be considered. Suppose, in the first place, that a hole appears at the required point without changing the density of the remainder of the system; *i.e.*, the expansion is transmitted through the whole of the solid. The behavior will then correspond to that postulated for viscous flow in a liquid, and increase of pressure will have an appreciable effect in retarding the rate of diffusion. In the second model, the necessary cavity for flow is made by compressing the neighboring molecules; as this stress gradually disappears with increasing distance from the hole, because of the crystalline structure, there would be relatively little expansion of the system as a whole. In this case the effect of pressure will arise chiefly from any modification of the structure of the solid that may be produced by pressure, and the diffusion coefficient may either increase or decrease; in any event the change may be expected to be relatively small. The limited experimental evidence indicates that the influence of pressure on diffusion in solids is very small, and hence the results favor the second of the models considered.

Effect of Concentration on Solid Diffusion.—The rate of diffusion in solids must be determined, as in liquid diffusion, by an activity rather than a concentration gradient. This is brought out by the fact that two solid solutions of very different composition may be in equilibrium with each other; *i.e.*, no diffusion takes place from one to the other. The effect of nonideality on diffusion in liquids has already been considered (page 530), and the same arguments are applicable to solids. If it is supposed that only one of the components of the system moves, Eq. (142) is applicable, *viz.*,

$$D_1 = D_1^0 \frac{d \ln a_1}{d \ln N_1} = \lambda^2 k \frac{d \ln a_1}{d \ln N_1}. \quad (164)$$

The data for confirming this relationship are meager, but a rough test may be made by plotting $\log a_1$, where the activity a_1 is determined from the ratio of the vapor pressure of the constituent of the system to that of the pure solid p_1/p_1^0 , against $\log N_1$ and comparing the curve so obtained with the plot of D against the mole fraction N_1 . The fact that curves of the same general form are obtained for the vapor pressures of zinc-copper alloys and for the diffusion of zinc into them may be taken as being in harmony with Eq. (164).

Diffusion of Gases in Metals.⁷⁰—The rates of diffusion of gases, particularly of hydrogen, have been studied in a number of instances; the values vary to a considerable extent with the nature of the metal, and this suggests that the process is a lattice diffusion, for diffusion along rifts or interfaces would probably be much less specific. The fact that the rate of diffusion has been found to be independent of grain size is evidence in favor of the same conclusion. At high gas pressures the rate of diffusion of hydrogen and other gases into metals is proportional to the square root of the pressure; this result suggests that the activated complex, and hence probably the dissolved gas, is in the form of atoms rather than of molecules (*cf.* page 387). If the activated state for diffusion were the molecule or two atoms associated together, the rate would be directly proportional to the gas pressure rather than to its square root. The square-root relationship appears difficult to reconcile with any mechanical picture of diffusion of molecules, and

⁷⁰ Stearn and Eyring, Ref. 64.

hence the view that atoms are involved may be regarded as established.

Deviations from the square-root dependence of the diffusion rate on pressure may be expected in two sets of circumstances. Diffusion of gas into the interior of a solid will presumably involve adsorption on the surface as a first stage; at very low pressures the rate of adsorption at the surface from which diffusion occurs may be slower than diffusion into the solid, and hence the former process will be rate-determining. It has been seen in Chap. VII that the rate of adsorption is in general proportional to the gas pressure, and so the same should be true, as found experimentally, for the over-all rate of diffusion at low pressures. As the pressure is increased, the rate of adsorption will increase proportionately; but that of the diffusion process, being dependent on the square root of the pressure, will increase less rapidly. It is clear that at a certain gas pressure the diffusion step will become rate-determining, and the over-all rate of diffusion will then be proportional to the square root of the pressure.

Deviations from the square-root relationship may also be expected when the surface is completely covered by adsorbed gas; the concentration of the activated state for diffusion, and hence the rate of diffusion under these circumstances, may be expected to be independent of the gas pressure. The same result will be obtained if the gas forms a compound on the surface of the metal; the rate of diffusion will then depend on the dissociation pressure of the compound, which is constant at a definite temperature, and not on the external pressure, provided that the latter is greater than the dissociation pressure. An instance of this type of behavior is the diffusion of oxygen through nickel at 900°C. at oxygen pressures in excess of 0.25 mm. of mercury.

Passage of Gases through Membranes.⁷¹—The diffusion of gases through membranes such as rubber, resins and plastics generally satisfies an equation of the type $D = A e^{-E/RT}$ and hence apparently involves the passage of the gas molecules from normal to activated states. In these circumstances, Eqs. (111) and (112) should be applicable, and $\lambda(e^{\Delta S^\ddagger/R})^{1/2}$ may be calculated

⁷¹ R. M. Barrer, *J. Chem. Soc.*, 278 (1934); *Trans. Faraday Soc.*, **35**, 628, 644 (1939).

by the method given on page 525. The results for a number of cases are recorded in Table LXXVIII. The large values for $\lambda(e^{\Delta S^\ddagger/R})^{1/2}$ in all these instances implies an appreciable entropy of activation, and hence it appears that diffusion through membranes of the plastic polymers is accompanied by the breaking of bonds in the latter. This conclusion finds support in the relatively high activation energies.

TABLE LXXVIII.—ENTROPY FACTORS FOR DIFFUSION OF GASES THROUGH PLASTICS

Gas	Membrane	A , cm. ² sec. ⁻¹	E , kcal.	$\lambda(e^{\Delta S^\ddagger/R})^{1/2}$ Å
H ₂	{ Butadiene-acrylonitrile polymer	56	8.70	182
N ₂		28	11.50	130
N ₂	Butadiene-methyl methacrylate polymer	37	11.50	150
H ₂	Neoprene	9.4	9.25	74
A	Neoprene	55	11.7	185
N ₂	Neoprene	78	11.9	215

It is of interest to record that for the diffusion of hydrogen and helium through silica and glass the quantity $\lambda(e^{\Delta S^\ddagger/R})^{1/2}$ is very small, *viz.*, approximately 0.04 Å. This means either that λ is much smaller than an atomic diameter or that activation is accompanied by a decrease in entropy, or both. It is difficult to see how an appreciable decrease of entropy could arise unless the activated state involved formation of a covalent bond between the diffusing gas and the membrane material; this is, of course, improbable for helium. Another possibility is that diffusion through the membrane was not the rate-determining step in the process.

ORIENTATION OF DIPOLES IN ELECTRIC FIELD

Time of Relaxation of Dipoles.—In general the dielectric constant of a substance is independent of the frequency of the electric field employed for its measurement, but under certain circumstances the phenomenon of "anomalous dispersion" of dielectric constant is observed; at a certain frequency, or rather within a small range of frequencies, the value of the measured dielectric

constant undergoes a rapid decrease. Anomalous dispersion occurs only with substances possessing a permanent dipole moment; although it has been observed with a number of liquids, both in the pure state and in solution, it is most easily detected in glasses or other highly viscous systems and in certain solids just below their melting points. The explanation of the anomalous dispersion of dielectric constant is based on the concept of the "time of relaxation of a molecule";⁷² this is the time required for the dipolar molecules to revert to random distribution after the removal of an electric field that has caused them to become oriented in a definite direction. It is evident that if the electric field has a relatively low oscillational frequency the dipoles will rotate fast enough for them to become completely oriented in every half cycle; but as the frequency is increased a value will be reached at which such orientation cannot occur, and the dielectric constant of the medium will fall. The theoretical treatment given by P. Debye,⁷³ based on the foregoing theory of dielectric relaxation, leads to the following equation for the molar polarization P :*

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \left(\alpha + \frac{\mu^2}{3kT} \cdot \frac{1}{1 + i\omega\tau} \right), \quad (165)$$

where ϵ is the dielectric constant of the medium, M the molecular weight, d the density, α the polarizability, μ the dipole moment and i the square root of -1 ; ω , the circular frequency, is equal to $2\pi\nu$, where ν is the oscillation frequency of the electric field, and τ is the relaxation time of the dipoles, as defined above; the symbols π , N , k and T have their usual significance. At high frequencies, for which the dielectric constant may be written ϵ_∞ , Eq. (165) becomes

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \alpha, \quad (166)$$

which is the usual equation for electron polarization; as is to be expected, under these conditions the orientation polarization

⁷² P. Debye, "Polar Molecules," Chap. V, Chemical Catalog Co., Inc., 1929.

⁷³ Debye, Ref. 72.

* In order to avoid confusion with the use of D for diffusion coefficient in previous sections of this chapter, it will be necessary to use ϵ here for the dielectric constant.

due to the permanent dipoles becomes zero, and the only contribution is the induced polarization. For low frequencies, on the other hand, Eq. (165) takes the familiar form

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \left(\alpha + \frac{\mu^2}{3kT} \right), \quad (167)$$

which is used for the determination of dipole moments; in between the high and low frequencies, there is the region of anomalous dispersion in which Eq. (165) must be employed. It has been shown by Debye that for such frequencies the dielectric constant ϵ may be regarded as made up of a real (ϵ') and an imaginary ($i\epsilon''$) part, *viz.*,

$$\epsilon = \epsilon' - i\epsilon''; \quad (168)$$

and it follows from Eqs. (165) to (168) that

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + x^2}, \quad (169)$$

and

$$\epsilon'' = \frac{\epsilon_0 - \epsilon_\infty}{1 + x^2} x, \quad (170)$$

where

$$x = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \omega\tau = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} 2\pi\nu\tau. \quad (171)$$

The values of ϵ' and ϵ'' for various frequencies can be derived from the measured dielectric constants; it is found that, in the region of normal dispersion, ϵ'' , which is a measure of the "dielectric loss," is very small. When anomalous dispersion becomes evident, however, the value of ϵ'' increases rapidly, reaches a maximum and then falls off again as the dielectric constant acquires its high-frequency value. It can be shown from Eq. (170) that ϵ'' will be a maximum when x is unity, and hence from (171)

$$\frac{1}{\tau} = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} 2\pi\nu_m, \quad (172)$$

where ν_m is the frequency for maximum dielectric loss; this is approximately in the middle of the region of anomalous dispersion. The dielectric constant at zero frequency (ϵ_0) is generally obtained by extrapolation, and the high-frequency

value (ϵ_∞) is taken as equal either to the dielectric constant in a solid at low temperatures, when there is no orientation of the dipoles, or to the square of the refractive index. It is thus possible to evaluate τ corresponding to maximum dielectric loss by means of Eq. (172), and this is regarded as the relaxation time of the molecules.

In the further development of the theory of dielectric relaxation, Debye regarded the rotation of the dipole in an electric field as equivalent to the rotation of a sphere in a viscous medium, and assuming Stokes's law for the frictional force acting on such a sphere the equation

$$\tau = \frac{4\pi\eta r^3}{kT}, \quad (173)$$

where η is the viscosity of the medium and r is the radius of the sphere, was deduced. This equation was found to be moderately satisfactory for a number of solutions and even for some pure liquids⁷⁴; but it is evident that it cannot be expected to hold in general for pure substances, on account of the intermolecular action, as well as for other reasons. This failure of Eq. (173) is made clear by a consideration of the results obtained with an isobutyl bromide glass. The relaxation time at 118.6°K. was found to be 0.9×10^{-6} sec.; if the value of r^3 is taken to be 16×10^{-24} cc., which cannot be seriously in error, the viscosity η , derived from Eq. (173), is 0.7×10^2 poises. The actual viscosity of the glass has not been measured at 118.6°K., but it is known that there is no discontinuity between liquid and glass; if the values for the viscosity of the former are extrapolated to 118.6°K., the result is 0.9 poise, *i.e.*, about 100 times smaller than that calculated from the relaxation time.⁷⁵ It is apparent, therefore, that the simple macroscopic viscosity is not the factor in terms of which it is possible to explain the hindrance to rotation of a dipolar molecule.

Application of the Theory of Absolute Reaction Rates.⁷⁶—The general conclusions given above concerning the variation of dielectric constant with frequency remain unaltered even if

⁷⁴ J. L. Oncley and J. W. Williams, *Phys. Rev.*, **43**, 341 (1933).

⁷⁵ W. O. Baker and C. P. Smyth, *J. Chem. Phys.*, **7**, 574 (1939).

⁷⁶ Eyring, Ref. 1; A. E. Stearn and H. Eyring, *ibid.*, **5**, 113 (1937); F. C. Frank, *Trans. Faraday Soc.*, **32**, 1634 (1936).

the concept of the relaxation time is changed in the following manner. Just as with viscosity and diffusion, it is convenient to regard dielectric relaxation as a rate process involving the rotation of the dipolar molecules about two mean equilibrium positions. It may be supposed that the molecules librate about one such position until they acquire the activation energy which permits them to pass over an energy barrier to the other. According to the theory of absolute reaction rates the number of times such a rotation will occur per second is given by

$$k = \frac{kT}{h} e^{-\Delta F^\ddagger/RT} \quad (174)$$

$$= \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}, \quad (175)$$

where ΔF^\ddagger , ΔH^\ddagger and ΔS^\ddagger represent, as usual, the standard free energy, heat change and entropy of activation. The average time required for a single rotation is $1/k$, and this may be identified with the so-called relaxation time τ , so that

$$\frac{1}{\tau} = \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}. \quad (176)$$

This equation is of the form

$$\frac{1}{\tau} = A e^{-E/RT}, \quad (177)$$

and so $\ln 1/\tau$ should be a linear function of $1/T$, as has been found to be the case. It is of interest to note that the values of the energy of activation for dipolar rotation obtained in this manner, *viz.*, at least 10.0 kcal. and generally very much greater (see Table LXXIX below), are considerably higher than the activation energies for viscosity, which are generally of the order of 2.0 kcal. and rarely more than 8 kcal. The treatment of dielectric relaxation as a rate process, therefore, leads to the same conclusion as that recorded above, that macroscopic viscosity is not adequate to account for the rotation of molecular dipoles in an oscillating electric field.

Valuable information concerning the nature of the rotation process may be obtained by dividing up the free energy of activation into its constituents, *i.e.*, the heat and entropy terms; ΔF^\ddagger is obtained from Eq. (174), ΔH^\ddagger from the variation of $\log 1/\tau$

with temperature and ΔS^\ddagger from the difference. The results for Permitol, a glassy substance consisting of isomers of tetrachlordiphenyl, in the temperature range from 281.7 to 307.7°K. are given in Table LXXIX.⁷⁷ It will be observed, in the first

TABLE LXXIX.—FREE ENERGY, HEAT AND ENTROPY OF ACTIVATION FOR DIPOLE ROTATION OF PERMITOL

Temp., °K.	$1/\tau$ sec. ⁻¹	A	ΔF^\ddagger , kcal.	ΔH^\ddagger , kcal.	ΔS^\ddagger , E. U.
281.7	3.69×10^3	2.3×10^{47}	12.5	56.5	156
289.9	6.41×10^4	8.1×10^{44}	10.6	53.2	147
298.5	6.79×10^6	3.8×10^{36}	9.2	42.0	110
307.7	4.49×10^6	1.7×10^{31}	7.9	34.6	87

place, that the entropies of activation are very large; this result implies that a large number of molecules surrounding the one which rotates are involved in the process of orientation. It is possible that the rotation of a single dipolar molecule requires some rearrangement of other molecules, a definite cooperation being necessary before the rotation can take place; the formation of the activated state will thus be accompanied by a considerable increase in entropy. It appears, therefore, that in some respects the rotation of a dipole in an electric field is similar to the rotation or other movement which brings about viscous flow in water at low temperatures (*cf.* page 505).

In spite of the high heat of activation, the effect of the large entropy increase is to make the free energy of activation relatively small; the value decreases with increasing temperature, suggesting a gradual change in the mechanism as the temperature is raised. At the higher temperatures the free energy of activation in Table LXXIX is not very much larger than is associated with viscous flow, and it may well be that eventually dipolar orientation and viscosity involve the same or similar activated states. This would account for the agreement sometimes found between the macroscopic viscosity and that calculated from Eq. (173). It is significant that in spite of the high activation energy for dipole orientation in Permitol a definite parallelism has been observed between the relaxation time and the viscosity

⁷⁷ *Cf.* Frank, Ref. 76; data from W. Jackson, *Proc. Roy. Soc.*, **135**, A, 158 (1935).

of the medium; this result suggests some fundamental connection between the ultimate mechanisms of orientation and flow.

The rotation of dipoles in isobutyl and isoamyl glasses is also accompanied by large entropy increases, as shown by the results in Table LXXX⁷⁸; the free energies of activation are,

TABLE LXXX.—DIPOLE ORIENTATION OF GLASSES

Substance	Temp., °K.	ΔF^\ddagger , kcal.	ΔH^\ddagger , kcal.	ΔS^\ddagger , E.U.
Isobutyl bromide.....	115.6	3.8	23.1	167
Isoamyl bromide.....	128.0	4.4	18.0	106

however, even smaller than those for Permitol. It is somewhat surprising to find that an increase of one CH_2 group causes such a marked change in the entropy of activation, as well as a considerable decrease in the heat of activation. It is suggested that the slight structural change is sufficiently anisotropic to make the isoamyl compound rotate preferably about its long axis only. If this is the case, the ratio of $\Delta E_{\text{vib.}}/E_{\text{vis.}}$ for isoamyl bromide should approach that of a long-chain molecule, whereas that for the isobutyl derivative should be smaller (page 494); the experimental results are 4.3 and 3.5, respectively, in general

TABLE LXXXI.—DIPOLE ORIENTATION OF WATER MOLECULES IN ICE

Temp., °K.	τ , sec.	ΔF^\ddagger , kcal.	ΔH^\ddagger , kcal.	ΔS^\ddagger , E.U.
227.3	$\sim 10 \times 10^{-5}$	9.1	~ 13.2	18.1
240.6	2.7×10^{-5}	9.0	~ 13.2	17.5
261.3	2.4×10^{-6}	8.5	~ 13.2	18.0
269.3	1.0×10^{-6}	8.4	~ 13.2	17.9
272.3	8.6×10^{-7}	8.4	~ 13.2	17.6

agreement with anticipation. Mention may be made of the fact that the free energies of activation for viscous flow in the two bromides under consideration are about 2.5 kcal., which is more than half the values for dipole orientation, although the heats of activation differ by a factor of at least 10.

In the cases already considered, dipolar rotation is accompanied by a large increase in the entropy of activation; but this

⁷⁸ Baker and Smyth, Ref. 75.

is not always true, for in the orientation of water molecules in ice there is only a small increase of entropy. The relaxation times, calculated in the usual manner from the dispersion of the dielectric constant, together with the free energy, heat and entropy of activation for the dipolar orientation of ice at temperatures not far below the melting point, are given in Table LXXXI.⁷⁹ It may be noted for purposes of comparison, that for viscous flow in water at 273°K., ΔF^\ddagger is approximately 3.8 kcal. and ΔH^\ddagger is 5.06 kcal. The heat of vaporization $\Delta E_{\text{vap.}}$ is about 10 kcal., at this temperature, and so the heat of activation for dipolar orientation is approximately of the order of the work required to make a hole of molecular size. Further reference to the subject of the rotation of the dipoles in water will be made in Chap. X in connection with the problem of the conductance of the hydrogen ion.

⁷⁹ Stearn and Eyring, Ref. 76.

CHAPTER X

ELECTROCHEMICAL PROCESSES

The passage of electricity through a solution and the deposition of material on the electrodes are both rate processes and hence should be susceptible of treatment, at least to some extent, by the methods used in the earlier chapters. The conductance of an electrolyte depends on the rate at which the ions travel through the solution, and the potential attained at an electrode when a metal or other substance is deposited at a definite rate equivalent to the current flowing is determined by the slow step in the processes involved in the discharge of an ion. Limited aspects only of these problems have been treated so far, but the discussion in the present chapter will indicate the applicability of the theory of absolute reaction rates to electrochemical processes.

ELECTROLYTIC CONDUCTANCE

Ionic Mobility.¹—In its simplest aspects the treatment of ionic mobility is similar to that of diffusion; as in Chap. IX, it is assumed that there is a series of equilibrium positions, and that passage of the moving unit, in this case an ion, from one position to another requires a certain activation energy. The full curve in Fig. 130 represents the change in free energy from an equilibrium position to an adjacent one separated from it by a distance λ ; if the concentration gradient is dc/dx then the concentrations at the two points are c and $c + \lambda dc/dx$, respectively. Suppose an electric field is now applied so that there is a potential gradient which facilitates the movement of the ion from left to right; the free-energy changes are now indicated by the dotted curve. The free energy in the initial state may be regarded as being increased by an amount αw , where w is the work done in moving the ion from one equilibrium state to the next and α is the fraction operative between the initial and activated states; similarly, the

¹ Cf. A. E. Stearn and H. Eyring, *J. Phys. Chem.*, **44**, 955 (1940).

free energy of the final state is diminished by $(1 - \alpha)w$, as shown in Fig. 130. The number of ions crossing the energy barrier in unit time in the forward direction, *i.e.*, in the direction of the applied field, is given by

$$\text{Rate in forward direction} = N\lambda ck e^{\alpha w/kT}, \quad (1)$$

where k , which is equal to $(kT/h) e^{-\Delta F^\ddagger/RT}$ [see Eq. (157), page 195], is the specific rate in either forward or backward direction, for an ideal system, in the absence of the field; N is the Avogadro

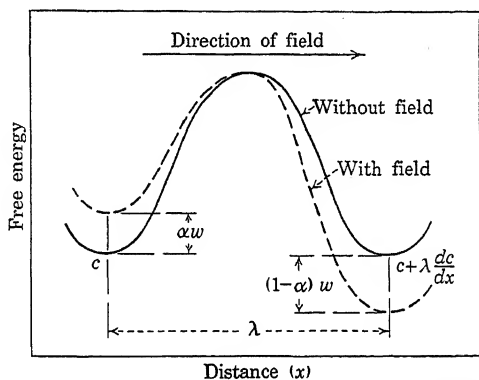


FIG. 130.—Free-energy curve for mobility of an ion with and without an applied electrical field.

number. The rate in the backward direction is given, in an analogous manner, by

$$\text{Rate in backward direction} = N\lambda \left(c + \lambda \frac{dc}{dx} \right) k e^{-(1-\alpha)w/kT}. \quad (2)$$

It will be observed that $e^{\alpha w/kT}$ appears in Eq. (1) because the electric field facilitates the movement of the ions in the forward direction, but since it retards migration in the opposite direction the term $e^{-(1-\alpha)w/kT}$ is employed in Eq. (2). Combination of Eqs. (1) and (2) then gives for the net rate of movement from left to right

$$\text{Net rate} = N\lambda ck e^{\alpha w/kT} - N\lambda \left(c + \lambda \frac{dc}{dx} \right) k e^{-(1-\alpha)w/kT}. \quad (3)$$

As a general rule, kT will be greater than w , and so in expanding

the exponentials it is permissible to drop all terms beyond the first power of w/kT ; Eq. (3) then becomes

$$\text{Net rate} = N\lambda ck \left(1 + \frac{\alpha w}{kT} \right) - N\lambda \left(c + \lambda \frac{dc}{dx} \right) k \left[1 - \frac{(1 - \alpha)w}{kT} \right] \quad (4)$$

$$= \frac{N\lambda ck w}{kT} - N\lambda^2 k \frac{dc}{dx} \left[1 - \frac{(1 - \alpha)w}{kT} \right] \quad (5)$$

It has already been assumed that $kT \gg w$, and so $(1 - \alpha)w/kT$ will be much less than, and hence can be neglected in comparison with, unity; upon making this approximation, Eq. (5) reduces to

$$\text{Net rate} = \frac{N\lambda ck w}{kT} - N\lambda^2 k \frac{dc}{dx} \quad (6)$$

If the potential gradient of the electrical field is ϕ , then the work done w in moving an ion of valence z , *i.e.*, carrying a charge $z\varepsilon$, where ε is the electronic charge, through a distance λ is given by

$$w = \lambda \phi z \varepsilon, \quad (7)$$

and insertion in Eq. (6) gives

$$\text{Net rate} = \frac{N\lambda^2 ck \phi z \varepsilon}{kT} - N\lambda^2 k \frac{dc}{dx} \quad (8)$$

It has been seen on page 519 that $\lambda^2 k$ is equal to the diffusion coefficient D , and hence Eq. (8) becomes

$$\text{Net rate} = \frac{NDc\phi z \varepsilon}{kT} - ND \frac{dc}{dx} \quad (9)$$

If the applied field causes appreciable movement of the ions, the second term on the right-hand side may be neglected in comparison with the first, so that

$$\text{Net rate} = \frac{ND_i c_i \phi z_i \varepsilon}{kT} \quad (10)$$

Since this equation is applicable strictly to a single ionic species, the suffix i has been added to the diffusion coefficient, concentration and valence. The number of ions transported in a

given direction by an applied potential gradient ϕ can also be expressed in terms of the ionic speed; if the latter is l_i for a potential gradient of unity, then

$$\text{Rate of transport of ions} = Nc_i l_i \phi, \quad (11)$$

and equating (10) and (11) gives

$$l_i = \frac{D_i z_i e}{kT}. \quad (12)$$

The equivalent conductance Λ_i of an ion is related to its speed under unit potential gradient by $l_i = \Lambda_i/F$, where F is the faraday²; further, Ns is equal to F and Nk is equal to R , and so it follows from Eq. (12) that

$$\Lambda_i = \frac{D_i z_i F^2}{RT}. \quad (13)$$

Diffusion Coefficient of an Electrolyte.—Even in the absence of an applied electrical field, a potential gradient will arise in the diffusion of an electrolyte if one ion travels faster than the other. In this case, it is not permissible to neglect the second term in Eq. (9), but it may be rewritten in the form

$$\text{Net rate of diffusion of } i\text{th ion} = \frac{ND_i c_i \phi z_i F}{RT} - ND_i \frac{dc}{dx} \quad (14)$$

$$= \frac{ND_i z_i F}{RT} \left(c_i \phi - \frac{RT}{z_i F} \cdot \frac{dc_i}{dx} \right) \quad (15)$$

$$= \frac{N\Lambda_i}{F} \left(c_i \phi - \frac{RT}{z_i F} \cdot \frac{dc_i}{dx} \right), \quad (16)$$

the value of Λ_i from Eq. (13) being introduced. The potential gradient ϕ , due to the difference in the speeds of the two ions, will operate in such a direction as to accelerate the slower moving ion and to retard the one that would move faster in the absence of a field; it follows, therefore, that the sign of the first term in the parentheses in Eq. (16) will be different for positive and negative ions. At equilibrium the two ions must diffuse at the same rate; supposing the positive ion to be the one with the

² See, for example, S. Glasstone, "The Electrochemistry of Solutions," 2d ed., D. Van Nostrand Company, Inc., p. 74, 1937.

* In this equation, R is expressed in volt-coulombs per degree since F is in coulombs and the potential gradient is in volts per centimeter.

higher diffusion coefficient, it follows from (16) that

$$\frac{N\Lambda_+}{F} \left(-c_+\phi - \frac{RT}{z_+F} \cdot \frac{dc_+}{dx} \right) = N\Lambda_- \left(c_-\phi - \frac{RT}{z_-F} \cdot \frac{dc_-}{dx} \right). \quad (17)$$

In the simplest case, *i.e.*, for a uni-univalent electrolyte, c_+ is equal to c_- , and hence

$$\frac{N\Lambda_+}{F} \left(-c\phi - \frac{RT}{F} \cdot \frac{dc}{dx} \right) = \frac{N\Lambda_-}{F} \left(c\phi - \frac{RT}{F} \cdot \frac{dc}{dx} \right); \quad (18)$$

$$-c\phi = \frac{RT}{F} \cdot \frac{dc}{dx} \cdot \frac{\Lambda_+ - \Lambda_-}{\Lambda_+ + \Lambda_-}. \quad (19)$$

The rate of diffusion of the electrolyte as a whole is equal to the equilibrium rate of diffusion of either ion, and the appropriate value is given by either side of Eq. (18); if the Avogadro number N is omitted, the result is the rate of diffusion in moles, instead of in molecules, per second. Inserting the value of $c\phi$ given by (19) in Eq. (18), the result is

Rate of diffusion of electrolyte in moles per second

$$= \frac{2RT}{F^2} \cdot \frac{\Lambda_+\Lambda_-}{\Lambda_+ + \Lambda_-} \cdot \frac{dc}{dx}. \quad (20)$$

Alternatively, the rate of diffusion may be written in terms of the diffusion coefficient [*cf.* Eq. (99), page 517], as

$$\text{Rate of diffusion} = -D \frac{dc}{dx}; \quad (21)$$

from Eqs. (20) and (21), it follows that

$$D = \frac{2RT}{F^2} \cdot \frac{\Lambda_+\Lambda_-}{\Lambda_+ + \Lambda_-}, \quad (22)$$

where D is the diffusion coefficient of the salt.

Equations (13) and (22) are identical in form with those derived by W. Nernst on the assumption that osmotic pressure is the driving force responsible for the diffusion of ions.³ The results obtained here are, of course, applicable to ideal solutions only, *i.e.*, for systems in which the activity coefficient is the same in successive equilibrium positions for diffusion. The

³ W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888); see also, M. Planck, *Ann. Physik*, **39**, 161, 561 (1890); R. Haskell, *Phys. Rev.*, **27**, 145 (1938).

correction for departure from ideal behavior could be made by the method described in Chap. IX; for solutions that are not too concentrated, the result, similar to Eq. (141) (page 533),

$$D = D_0 \left(1 + \frac{d \ln \gamma}{d \ln N} \right), \quad (23)$$

would be obtained, D_0 being the diffusion coefficient for the ideal solution and γ the activity coefficient of the electrolyte in a solution containing a mole fraction N of solute. Equation (23) is analogous to those derived in a different manner by L. Onsager and R. M. Fuoss.⁴ It may be mentioned, without going into details, that Eqs. (22) and (23) are in general agreement with experiment; the former gives the diffusion coefficient of an electrolyte in dilute solution and the latter represents the variation of the coefficient with concentration.⁵

Ionic Mobility and Viscosity.—The fact that the activation energies, calculated from the ionic mobilities, of most ions in a given solvent are the same, *e.g.*, 4.0 to 4.2 kcal. in water at 25°C., and that the values are almost identical with that for viscous flow of the solvent, suggests that the rate of migration of an ion in an applied field is determined by the solvent molecules jumping from one equilibrium position to the next. Since the molecules of solvent have to move in the intense electric field of the ions, it is probable that the free energy of activation will not be the same as for viscous flow of the pure solvent; the value of k , the specific rate constant for the movement of an ion, will therefore differ to some extent from that for viscosity. The difference is likely to be greater the smaller the ion and the higher its charge, *i.e.*, the more intense the electric field in its immediate vicinity. The approximation can be made, however, of regarding k for ionic diffusion, either natural or under the influence of an applied potential gradient, to be the same as the corresponding quantity for the flow of the solvent, as on page 519. Further, if the ions are not too large in comparison with the molecules of solvent, the values of λ will be nearly equal for both cases; it is then possible to introduce into Eq. (13) the following relationship between the diffusion coefficient D

⁴ L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2687 (1932).

⁵ Cf. A. R. Gordon *et al.*, *J. Chem. Phys.*, **5**, 522 (1937); **7**, 89, 963 (1939); see also P. van Rysselberghe, *J. Am. Chem. Soc.*, **60**, 2326 (1938).

of the ion and the viscosity η of the medium [cf. Eq. (106), page 519], *viz.*,

$$D_i = \frac{\lambda_1}{\lambda_2 \lambda_3} \cdot \frac{kT}{\eta}, \quad (24)$$

with the result

$$\Lambda_i \eta = \frac{\lambda_1}{\lambda_2 \lambda_3} \cdot \frac{kz_i F^2}{R} \quad (25)$$

It should be noted that k is here expressed in ergs per degree while R is in volt-coulombs, *i.e.*, joules, per degree so that k/R is equal to 1.66×10^{-17} ; since F is 96,500, it follows that

$$\Lambda_i \eta = 1.55 \times 10^{-7} \frac{\lambda_1}{\lambda_2 \lambda_3} z_i. \quad (26)$$

The term $\lambda_2 \lambda_3 / \lambda_1$ for self-diffusion in water (page 521) is known to be about 1.4×10^{-7} , and so it follows that $\Lambda_i \eta$ should be of the order of unity; this is in general agreement with observation (see Table LXXXII).

If allowance were made for the fact that the specific rate constant for ionic diffusion is somewhat less than that for viscous flow of the solvent, because of the increased free energy of activation resulting from the electric field of the ion, the value of $\Lambda_i \eta$ would be somewhat smaller than is given by Eq. (26) and would, consequently, be in even better harmony with the experimental results. Introduction of the treatment for the diffusion of large particles given on page 519, which is also applicable to the migration of large ions, would also lead to a value of $\Lambda_i \eta$ smaller than that required by Eq. (26).

Since the factor $\lambda_1 / \lambda_2 \lambda_3$ will not differ appreciably from one solvent to another, it is evident that the product $\Lambda_i \eta$ should be approximately constant for a given ion, irrespective of the nature of the solvent*; this is in fact the rule proposed by P. Walden⁶ and generally referred to by his name. It is true that for many ions, especially those of large size, the value of

* According to Stokes's law or to the results derived on p. 519 for large particles, the product $\Lambda_i \eta$ should be precisely constant in all solvents, provided that the radius of the ion remains unchanged.

⁶ P. Walden, *Z. physik. Chem.*, **55**, 207, 246 (1906); "Salts, Acids and Bases, etc.," McGraw-Hill Book Company, Inc., p. 283, 1929.

$\Delta\eta$ is approximately constant in a number of solvents;⁷ as might be anticipated from the discussion above, the $\Delta\eta$ product is not completely independent of the nature of the solvent.

In certain instances, further, very marked deviations from Walden's rule have been observed, and these require special explanation. A particular instance of abnormal behavior is provided by the hydrogen ion, as may be seen by comparing the results in Table LXXXII for the product $\Delta\eta$ for hydrogen and sodium ions at 25°C.

TABLE LXXXII.—ION CONDUCTANCE-VISCOSITY PRODUCTS IN VARIOUS SOLVENTS

Solvent	H ₂ O	CH ₃ OH	C ₂ H ₅ OH	CH ₃ ·CO·CH ₃	CH ₃ NO ₂
Hydrogen ion....	3.14	0.78	0.67	0.28	0.36
Sodium ion.....	0.45	0.26	0.20	0.22	0.36

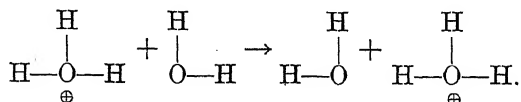
It is apparent that although the conductance-viscosity product for the sodium ion is almost constant, except for the somewhat higher value in water, the values for the hydrogen ion are abnormally high in hydroxylic solvents and especially in water; this is in harmony with the fact that the conductance of the hydrogen ion in water is greater than that of any other ion, except the hydroxyl ion, by a factor which generally exceeds 5. It may be mentioned, too, that, although most ions have an activation energy for ionic mobility of about 4 kcal. in water at 25°, that for the hydrogen ion is only 2.8 kcal. It is evident, therefore, that the migration of the hydrogen ion through aqueous solution involves a mechanism different from that applicable to other ions.

Abnormal Ionic Mobilities.—The exceptionally high mobility of the hydrogen ion in hydroxylic solvents and particularly in water has long attracted interest, and the possibility of a type of Grotthuss chain conduction was suggested many years ago to account for the abnormal value.⁸ This point of view has been developed more explicitly in recent times, by utilizing

⁷ Cf. H. Ulich, *Fortschritte der Chemie, Physik und physikalische Chemie*, **18**, [10] (1926); *Trans. Faraday Soc.*, **23**, 388 (1927).

⁸ See, for example, H. Danneel, *Z. Elektrochem.*, **11**, 249 (1905); A. Hantzsch and K. S. Caldwell, *Z. physik. Chem.*, **58**, 575 (1907).

modern ideas concerning the structure of water and the nature of the hydrogen ion in solution.⁹ It is probable that at ordinary temperatures each oxygen atom in water is surrounded, on the average, by four hydrogen atoms disposed in an approximately tetrahedral manner. Two of these hydrogen atoms may be regarded as belonging to a particular oxygen atom and are at a distance of about 0.95 Å. from it, whereas the other two, which belong to other oxygen atoms, are about 1.81 Å. away. The higher the temperature the less is this structure maintained, the disorder increasing as the temperature is raised. Ionization results when one of the two more distant hydrogen atoms comes 0.86 Å. closer to an oxygen atom, so that there are now three hydrogen atoms at a distance of 0.95 Å. from the central atom whereas the fourth is at a farther distance. The hydrogen ion is thus to be represented by H_3O^+ , although it is still part of the structure of the water. Transfer of the hydrogen atom—or, more correctly, a proton—from one water molecule to another leaves the oxygen atom of the former molecule with one close and three distant hydrogen atoms, and this constitutes the OH^- ion. When water contains an acidic substance, *e.g.*, hydrochloric acid, in solution, the H_3O^+ ions that are formed are believed to fit into the structure just as well as in pure water, and the interatomic distances can, as an approximation, be regarded as unchanged. When a potential is applied, it is supposed that the H_3O^+ ions travel through the solution to some extent in the ordinary diffusion manner, involving passage of solvent molecules over an energy barrier from one equilibrium position to another, as considered above; but in addition there is another mechanism that permits of a more rapid ionic transport. This involves the transfer of a proton from an H_3O^+ ion to an adjacent water molecule, the proton moving through a distance of 0.86 Å. and thus forming another H_3O^+ ion, as follows:



⁹ E. Hückel, *Z. Elektrochem.*, **34**, 546 (1928); J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933); C. Wannier, *Ann. Physik*, **24**, 545, 569 (1935).

The resulting H_3O^+ ion can now transfer a proton to another water molecule, and in this way the positive charge will be transferred a considerable distance in a short time; hence, the hydrogen ion acquires an exceptionally high conductivity. It will be observed that after the passage of the proton the water molecules are oriented in a manner different from that which existed while the proton was being transferred. If the prototropic process of conduction is to continue, therefore, each water molecule must rotate after the proton has been passed on, so that it may be ready to receive another proton coming from the same direction. The combination of proton transfer and rotation of the water molecules can thus account for the abnormal conductance of the hydrogen ion in aqueous solution.

Absolute-reaction-rate Theory.¹⁰—A complete theoretical treatment of the rate of proton transfer would involve a calculation by means of quantum mechanics of the height of the energy barrier over which the proton has to pass in going from a hydrogen ion to a water molecule, but such a procedure is too difficult to carry out for the complicated system involved. The method employed here, therefore, is to calculate the mobility as a function of the barrier height and then to determine this height from the experimental mobilities.

The passage of a proton over an energy barrier has been discussed by several authors, and it was at one time suggested that the exceptional mobility of the hydrogen ion was due, in part, to quantum-mechanical leakage, or "tunneling," through a thin barrier.¹¹ If this were the case, the mobility of the deuterium ion D_3O^+ should be very much smaller than that of H_3O^+ since the extent of tunneling would be greatly diminished. Actually, the conductivity of the deuterium ion is also abnormally high, although not so large as that of the corresponding hydrogen ion. It appears, therefore, that the energy barrier is relatively flat; hence, it can be treated classically, the quantum-mechanical leakage being neglected.

Before applying the theory of absolute reaction rates to the problem of the conductance of the hydrogen ion, there are two points to consider: (1) the magnitude of the mobility due to the prototropic change, and (2) the nature of the slow process. The

¹⁰ A. E. Stearn and H. Eyring, *J. Chem. Phys.*, **5**, 113 (1937).

¹¹ Bernal and Fowler, Ref. 9.

abnormal contribution to the conductance may be taken as the difference between the measured value for the hydrogen ion and an estimated amount due to the normal diffusion transfer. It has been suggested that the latter may be taken as equal to the ionic conductance of the sodium ion in the same solvent,¹² and this view receives support from the fact that in media such as acetone and nitromethane, in which hydrogen ions have a normal conductivity, the values are very similar for sodium and hydrogen ions (Table LXXXII). On this basis the prototropic contribution to the conductance of H_3O^+ ions is $349.9 - 50.9 = 299.0$ reciprocal ohms at 25°C . There is reason for believing that of the two processes involved in this type of conduction, *viz.*, proton transfer and rotation of the water molecules, the former is rate-determining.

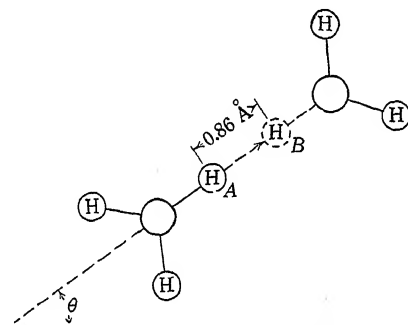


FIG. 131.—Transfer of a proton from a hydrogen ion (H_3O^+) to a water molecule.

Transfer of Protons.—The model representing the proton transfer from one water molecule to another is depicted in Fig. 131; the proton that moves is initially in the position A and finishes in the position B, and hence it is regarded as moving through the shortest possible distance, *i.e.*, 0.86 \AA , without disturbing the oxygen atoms. In order to make the argument general, it is supposed that the O—H linkage, the length of which is increased as the result of the proton transfer, is inclined at an angle θ to the applied field. The potential barrier over which the proton has to pass is shown in Fig. 132, in which the full line represents the change in standard free energy in passing

¹² Hückel. Ref. 9.

from initial to final states in the absence of an applied field and the dotted curve corresponds to the conditions when the field is operating. The specific rate of transfer of protons in any given direction will be, according to the theory of absolute reaction rates,

$$k = \frac{kT}{h} e^{-\Delta F^\ddagger/RT}, \quad (27)$$

the transmission coefficient being taken as unity. Since the process takes place equally in all directions, there is no net transfer of protons. When a field having an *effective* potential gradient of ϕ is applied, the specific reaction rate at an angle θ to the direction of the field, *i.e.*, as shown in Fig. 131, is given by

$$k = \frac{kT}{h} e^{-(\Delta F^\ddagger - \delta F^\ddagger)/RT}, \quad (28)$$

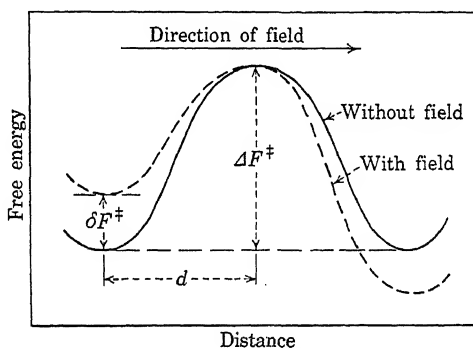


FIG. 132.—Free-energy curve for the transfer of a proton with and without an applied electrical field.

where δF^\ddagger is defined by

$$\delta F^\ddagger = \phi \cos \theta \times d \times 23,060; \quad (29)$$

d is one-half the distance across the barrier, *i.e.*, $\frac{1}{2} \times 0.86 = 0.43$ Å., and the factor 23,060 converts electron-volts into calories. Upon inserting the value of δF^\ddagger given by Eq. (29) into (28), it is seen that

$$k = \frac{kT}{h} e^{-\Delta F^\ddagger/RT} e^{a \cos \theta}, \quad (30)$$

where

$$a = \phi \times 0.43 \times 10^{-8} \times \frac{23,060}{RT} \quad (31)$$

$$= 0.50 \times 10^{-4} \times \frac{\phi}{T}. \quad (32)$$

Since the rotation of the molecules probably occurs rapidly, in comparison with the process under consideration, a proton in crossing the potential barrier has virtually traveled the distance from one oxygen atom to a position on the further side of an adjacent oxygen atom. This distance may be taken as the average dimensions of a water molecule in any direction, and thus may be estimated by dividing the molecular volume of water by the Avogadro number, to give the mean volume of a single water molecule, and extracting the cube root, *i.e.*,

$$\left(\frac{18}{6.023 \times 10^{23}} \right)^{1/3} = 3.1 \times 10^{-8} \text{ cm.}$$

It follows, therefore, that for every proton which crosses the energy barrier a unit positive charge is transferred through a distance of 3.1×10^{-8} cm. The distance traveled in the direction of the field is $3.1 \times 10^{-8} \cos \theta$, and hence the total distance covered per second by all the protons that pass over the barrier is obtained when the specific rate, given by Eq. (30), is multiplied by this distance; thus,

Distance traveled in direction of field

$$= 3.1 \times 10^{-8} \times \cos \theta \frac{kT}{h} e^{-\Delta F^\ddagger/RT} e^{a \cos \theta} \text{ cm. sec.}^{-1} \quad (33)$$

This process takes place in all directions, including directions opposite to the field, and hence it is necessary to take the average over all angles θ in order to obtain the net distance moved in the direction of the field per second; *i.e.*,

Rate of transfer = 3.1×10^{-8}

$$\times \frac{kT}{h} e^{-\Delta F^\ddagger/RT} \frac{\int_0^\pi e^{a \cos \theta} \cos \theta \sin \theta d\theta}{\int_0^\pi \sin \theta d\theta} \text{ cm. sec.}^{-1} \quad (34)$$

For all reasonable values of ϕ , the quantity a will be very small [cf. Eq. (32)], and so it is possible to write

$$e^{a \cos \theta} \approx 1 + a \cos \theta, \quad (35)$$

and hence

Rate of transfer

$$= 3.1 \times 10^{-8} \times \frac{kT}{h} e^{-\Delta F^\ddagger/RT} \frac{\int_0^\pi (1 + a \cos \theta) \cos \theta \sin \theta d\theta}{\int_0^\pi \sin \theta d\theta} \quad (36)$$

$$= 3.1 \times 10^{-8} \times \frac{kT}{h} e^{-\Delta F^\ddagger/RT} \cdot \frac{a}{3} \text{ cm. sec.}^{-1} \quad (37)$$

This expression applies to each proton of the H_3O^+ ion; but since there are three protons that can move, the result should be multiplied by 3, *i.e.*,

$$\text{Rate of transfer} = 3.1 \times 10^{-8} \times \frac{akT}{h} e^{-\Delta F^\ddagger/RT}. \quad (38)$$

The equivalent conductance of any ion is equal to the speed in cm. per second multiplied by the faraday, 96,500 coulombs (*cf.* page 555); and hence the abnormal contribution Λ' to the conductance of the hydrogen ion will be given by

$$\Lambda' = 3.1 \times 10^{-8} \times 9.65 \times 10^4 \times 0.50 \times 10^{-4} \times \frac{\phi}{T} \cdot \frac{kT}{h} e^{-\Delta F^\ddagger/RT} \quad (39)$$

$$= 3.12 \times 10^3 \times \phi e^{-\Delta F^\ddagger/RT}. \quad (40)$$

Since Λ' can be derived from experimental data on the conductances of hydrogen and sodium ions, as previously explained, it is possible by the aid of Eq. (40) to calculate $\Delta F^\ddagger - RT \ln \phi$ for various temperatures; the results are given in the third column of Table LXXXIII (see page 566).¹³

In order to evaluate ΔF^\ddagger itself, it is necessary to know ϕ , the *effective* potential gradient between a hydrogen ion and a water molecule when the over-all potential gradient is 1 volt/cm., the latter being the value assumed in the calculation of the ion conductance. It has been suggested¹⁴ that

$$\phi = \frac{D + 2}{3}, \quad (41)$$

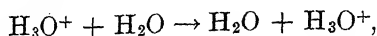
where D is the dielectric constant at the experimental tempera-

¹³ Stearn and Eyring, Ref. 10.

¹⁴ Hückel, Ref. 9.

ture, and by using this relationship the results for ΔF^\ddagger given in the fourth column of Table LXXXIII were obtained.

The entropy change of the over-all process



including rotation, will be zero; but it is reasonable to suppose that there will be some restriction in the activated state for proton transfer, so that the entropy of activation for the rate-determining stage will be negative. If this is the case, the heat of activation ΔH^\ddagger should be less than the free energy ΔF^\ddagger . Exper-

TABLE LXXXIII. ABNORMAL CONDUCTANCE OF THE HYDROGEN ION

Temp., °K.	Δ'	$\Delta F^\ddagger - RT \ln \phi$, cal.	ΔF^\ddagger , cal.	ΔH^\ddagger , cal.
273	196.5	1,508	3,350	
291	270.5	1,431	3,349	2,822
298	299	1,409	3,355	2,482
323	383	1,352	3,389	1,907
348	449	1,346	3,462	1,430
373	489	1,389	3,573	886
401	519	1,435	3,684	636
429	528	1,521	3,811	211

imental values of ΔH^\ddagger , derived from the variation of Δ' with temperature, are recorded in Table LXXXIII. It appears that the decrease in entropy accompanying the formation of the activated state increases with increasing temperature; this is not unexpected in view of the greater randomness in the structure of the solution, *i.e.*, the initial state, at the higher temperatures.

Comparison of the Two Stages.—The assumption that the transfer of a proton from an H_3O^+ ion to a molecule of water is the rate-determining stage in the abnormal conductance has led to a value for the free energy of activation of the process of about 3,500 cal. (Table LXXXIII); and comparison of this figure with that obtained for rotation of a water molecule in ice at 0°C., *viz.*, 8,400 cal. (see page 550) would suggest, at first sight, that the rotation might, in fact, be the slow process. It must be remembered, however, that there is a considerable difference in the concentrations of hydrogen ions and water molecules in water. It can be shown from the ionic product that, in pure

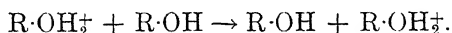
water at 0°C., $c_{\text{H}_3\text{O}^+}/c_{\text{H}_2\text{O}}$ is equal to $e^{-11,350/RT}$, which is considerably smaller than the factor arising from the difference of 4,900 cal. in the free energies of activation. It appears to be established, therefore, that in pure water, at least, rotation is the faster process and the prototropic change is rate-determining; the same general conclusion is, presumably, applicable to all aqueous solutions.

Influence of Solvent on Abnormal Conductance of Hydrogen Ion.—The values of Λ_H in Table LXXXII indicate that the appropriate hydrogen ion, *viz.*, MeOH_2^+ and EtOH_2^+ , is abnormally mobile in methyl and ethyl alcohol solutions, respectively. This fact is seen more clearly from a comparison of the actual ion conductances of hydrogen and sodium ions in these media; the data are recorded in Table LXXXIV, where Λ_H is the conductance of the hydrogen ion and Λ' is the difference between

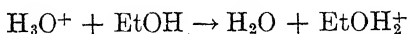
TABLE LXXXIV.—ION CONDUCTANCES AT 25°C.

Solvent	Λ_H	Λ_{Na}	Λ'
MeOH	142	45.7	96.3
EtOH	59.5	18.7	40.8
(D ₂ O)	242.4	41.5	200.9)

the values for hydrogen and sodium ions and so represents the abnormal contribution. The values for deuterium oxide are also included. The abnormal conductance may be attributed to a prototropic change, just as in aqueous solution, *viz.*,



It is of interest to record that in the presence of a small quantity of water the hydrogen ion is not abnormally mobile in alcoholic solution, the conductance of H_3O^+ in ethyl alcohol being 16.8, as compared with 18.7 reciprocal ohms for the sodium ion.¹⁵ It is true that the proton-transfer process



is possible; but it is known from equilibrium data that the rate

¹⁵ H. Goldschmidt, *Z. physik. Chem.*, **89**, 129 (1914). The difference between the equivalent conductances of $\text{C}_2\text{H}_5\text{OH}_2^+$ and H_3O^+ in ethyl alcohol is given as 42.7 reciprocal ohms.

of the reverse reaction very greatly exceeds that of the forward reaction, and so the transfer of protons by this mechanism will occur to a negligible extent only. Since most of the hydrogen ions are present in the form of H_3O^+ , the abnormal conductance in these circumstances will not be appreciable. As the amount of water is increased, it will be increasingly possible for the proton to pass from H_3O^+ to H_2O , and the abnormal mobility will become evident. Similarly, in pure alcohol, in the absence of water, the passage of protons from EtOH_2^+ ions to EtOH molecules will result in an increase of conductance.

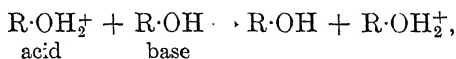
Prototropic Change and Acid-Base Catalysis.¹⁶—The proton-transfer process responsible for the abnormal conductance of the hydrogen ion is analogous to the rate-determining prototropic change involved in general acid and base catalysis. For reactions of the latter type the relationship (*cf.* page 467)

$$k = GK^x, \quad (42)$$

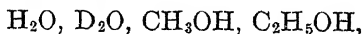
or

$$\log k = \log G + x \log K, \quad (43)$$

is applicable, where k is the specific reaction rate, K the dissociation constant of the acid that provides, or the base that removes, the proton, and G and x are characteristic constants for each substrate. In the prototropic reactions under consideration, *e.g.*,



a similar relationship might be expected to apply between the rate of the reaction, as measured by the abnormal contribution to the conductance, and the dissociation constant either of the acid $\text{R}\cdot\text{OH}_2^+$ or of the base $\text{R}\cdot\text{OH}$. It does not appear to be possible to decide a priori whether to regard the rate of the process as being determined by the acid or the base, for this will depend on the relative influences of the energy of breaking the $\text{O}-\text{H}$ bond in the acid and the repulsion between the proton and the base. A decision can be made, however, from the experimental fact that in the series



¹⁶ E. C. Baughan, unpublished.

the dissociation constant of $R\cdot OH$ as a base, *i.e.*,

$$a_{R\cdot OH_2^+} \times a_{OR^-} / a_{R\cdot OH},$$

varies by a factor of 20,000 whereas that of the corresponding acid $R\cdot OH_2^+$, *i.e.*, $a_{R\cdot OH_2^+} \times a_{R\cdot OH} / a_{R\cdot OH_2^+}$, alters by a factor of approximately 3. It appears, therefore, that the strength of the base is the determining factor; and hence the relationship, similar to Eq. (43), *viz.*,

$$\log \Lambda' = \text{const.} + x \log K, \quad (44)$$

where Λ' is the abnormal conductance and K is the dissociation constant of the solvent molecule as a base, might be expected to apply. The experimental values of $\log \Lambda'$ are plotted against

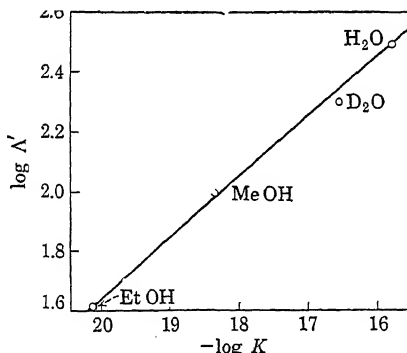


FIG. 133.—Dependence of abnormal conductance of the hydrogen ion on the dissociation constant of the solvent as a base. (*Baughan.*)

$-\log K$, in Fig. 133, and the results are seen to fall approximately on a straight line which can be represented by the equation

$$\log \Lambda' = 5.54 + 0.193 \log K. \quad (45)$$

It was seen in Chap. VIII (page 469) that for a series of reactions to which the Brønsted relationship was applicable the difference in the heats of activation ΔH^\ddagger could be regarded as approximately equal to a fraction x of the difference in the heats of the complete reaction ΔH , *i.e.*,

$$\Delta H_1^\ddagger - \Delta H_2^\ddagger = x(\Delta H_1 - \Delta H_2). \quad (46)$$

From the temperature coefficients of the mobilities of H_3O^+ and D_3O^+ , it appears that, for these two ions, $\Delta H_1^\ddagger - \Delta H_2^\ddagger$ is 230 cal.

On the other hand, the difference in the heats of ionization, which may be taken as $\Delta H_1 - \Delta H_2$, is 940 cal.; and if x is 0.193 as given by Eq. (45), it follows that $x(\Delta H_1 - \Delta H_2)$ is 180 cal., in fair agreement with the value of 230 cal. obtained directly.

Influence of Pressure on the Abnormal Mobility of Hydrogen Ion.¹⁷—Equation (39) for the abnormal conductance of the hydrogen ion in water may be written in the form

$$\Lambda' = A e^{-\Delta F^\ddagger/RT}; \quad (47)$$

and it can be seen from Eqs. (31) and (39) that apart from constant quantities the term A is the product of two lengths, one being half the distance 0.86×10^{-8} cm., averaged over all

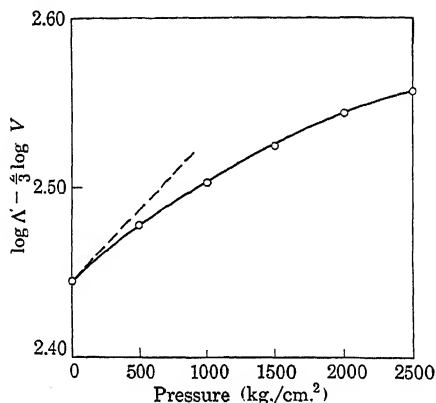


FIG. 134.—Dependence of abnormal conductance of the hydrogen ion on pressure. (Baughan.)

values of θ and the other the average distance 3.1 \AA. between neighboring oxygen atoms. It is therefore permissible to write

$$A = \text{const.} \times V^{2/3}, \quad (48)$$

where V is the specific volume of water, and so

$$\Lambda' = \text{const.} \times V^{2/3} e^{-\Delta F^\ddagger/RT}. \quad (49)$$

Upon taking logarithms of Eq. (49) and differentiating with respect to pressure, it is seen that

$$\left(\frac{\partial \ln \Lambda'}{\partial p} \right)_T = \frac{2}{3} \left(\frac{\partial \ln V}{\partial p} \right)_T - \frac{1}{RT} \left[\frac{\partial (\Delta F^\ddagger)}{\partial p} \right]_T. \quad (50)$$

¹⁷ Baughan, Ref. 16.

The expression $\partial(\Delta F^\ddagger)/\partial p$ may be replaced by its thermodynamic equivalent ΔV^\ddagger , *i.e.*, the increase in volume accompanying the formation of the activated state (page 470); hence, Eq. (50) may be rewritten in the form

$$\frac{\partial}{\partial p} (\ln \Lambda' - \frac{2}{3} \ln V) = - \frac{\Delta V^\ddagger}{RT}. \quad (51)$$

If ΔV^\ddagger is independent of pressure, it is seen that the plot of $\ln \Lambda' - \frac{2}{3} \ln V$ against p should give a straight line; the experimental results are quoted in Table LXXXV and are plotted in Fig. 134. The values of Λ' are obtained from the difference in the equivalent conductances of hydrochloric acid and sodium chloride at infinite dilution.

TABLE LXXXV.—INFLUENCE OF PRESSURE ON ABNORMAL CONDUCTANCE AT 20°C.

Pressure, kg./cm. ²	Λ' , recip. ohms	V , cc.	$\log \Lambda' - \frac{2}{3} \log V$
1	278.6	1.0000	2.445
500	295.0	0.9766	2.447
1,000	310.0	0.9582	2.503
1,500	322.9	0.9421	2.526
2,000	334.7	0.9257	2.546
2,500	345.0	0.9134	2.564

The actual plot is seen to be a curve, rather than a straight line, which suggests that ΔV^\ddagger is a function of pressure; the initial tangent gives ΔV^\ddagger at small pressures, and this is found to be -4 cc. per mole. Of this amount, 2.9 cc. arises from the increase of $\ln \Lambda'$ with pressure and 1.1 cc. from the change in $\ln V$.

The general equation (43) may be regarded as equivalent to the relationship

$$\Delta F_1^\ddagger - \Delta F_2^\ddagger = x(\Delta F_1 - \Delta F_2), \quad (52)$$

where the ΔF terms are the free-energy changes for the complete reaction; hence, it also follows that

$$\frac{\partial(\Delta F^\ddagger)}{\partial p} = x \frac{\partial(\Delta F_i)}{\partial p} = x \Delta V_i, \quad (53)$$

where ΔV_i is the increase in molar volume accompanying ioniza-

tion. Since $\partial(\Delta F^\ddagger)/\partial p$ is equal to ΔV^\ddagger , it follows that

$$\Delta V^\ddagger = x \Delta V_i, \quad (54)$$

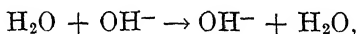
where x has the same value as in Eq. (45), *i.e.*, 0.193. The volume change accompanying the ionization of water at room temperatures and at atmospheric pressure is -21 cc. per mole; and hence, according to Eq. (54), ΔV^\ddagger should be -0.193×21 , *i.e.*, -4.05 cc. per mole, in excellent agreement with the result obtained from Fig. 134.

Abnormal Mobilities of Other Ions.—In addition to the hydrogen ion, the hydroxyl ion exhibits abnormal conductance in water, but the corresponding ions, *viz.*, OMe^- and OEt^- , in methyl and ethyl alcohols, do not show this behavior. This is exemplified by the results in Table LXXXVI which include the values for the chloride ion to be used for purposes of comparison.

TABLE LXXXVI.—IONIC CONDUCTANCES OF ANIONS

Solvent	Ion	Λ	Λ_{Cl^-} , recip. ohms
Water.....	OH^-	200	75
Methyl alcohol.....	OMe^-	53.3	51.3
Ethyl alcohol.....	OEt^-	24.5	24.3

The abnormal conductance of the OH^- ion may be accounted for by the prototropic process



a proton being transferred from a water molecule to an hydroxyl ion, in a manner exactly analogous to that involved in connection with hydrogen ions. By the same argument, some abnormal mobility might be expected for the OMe^- and OEt^- ions; but it can be shown that the effects should be relatively small in these instances. If the abnormal conductances vary with the dissociation constant of $\text{R}\cdot\text{OH}$ in the same manner as do those of the corresponding hydrogen ions,¹⁸ it follows that

$$\frac{\Lambda'_{\text{OH}^-}}{2 \times \Lambda'_{\text{OR}^-}} = \frac{2 \times \Lambda'_{\text{H}^+\text{O}^+}}{3 \times \Lambda'_{\text{R}\cdot\text{OH}_2^+}}, \quad (55)$$

¹⁸ Baughan, Ref. 16.

the weighting factors allowing for the different numbers of protons available in each case. The abnormal mobilities of OMe^- and OEt^- should then be 30 and 12 reciprocal ohms, respectively; these calculated values are probably too large.

Types of Grotthuss Mechanism.—It can be seen that, in general, abnormal ionic mobilities are to be anticipated whenever there exists in solution the possibility of a prototropic or anionotropic change (see below) of the type considered in this chapter. It is important to note, however, that the possibility of such a process is not a sufficient condition for abnormal mobility; it is necessary, in addition, that the transfer of the proton or anion shall be able to take place with a relatively high speed. In the case of proton transfer, this appears to be determined by the dissociation constant of the solvent molecule as a base.

Three types of Grotthuss mechanism leading to abnormal conductance may be distinguished:

1. Transfer of a proton or a deuteron from a positive ion to a neutral molecule.
2. Transfer of a proton or a deuteron from a neutral molecule to a negative ion.
3. Transfer of a charged unit other than a proton or a deuteron.

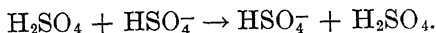
The abnormal mobilities of H_3O^+ and D_3O^+ in H_2O and D_2O , respectively, and of the $\text{R}\cdot\text{OH}_2^+$ ions in the corresponding alcohols fall into class 1; and, as already seen, the effects can be correlated with the strengths of the solvent as a base, in accordance with the requirements of the Brønsted relationship. It is probable that the absence of abnormal mobility of the NH_4^+ ion in ammonia and of the anilinium, pyridinium and *m*-chloranilinium ions in the respective amines can be accounted for in an analogous manner by the low self-dissociation constants, *i.e.*,

$$a_{\text{R}\cdot\text{NH}_3^+} \times a_{\text{R}\cdot\text{NH}^-} / a_{\text{R}\cdot\text{NH}_2},$$

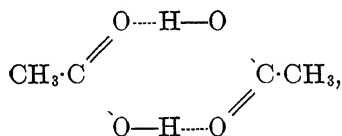
of the free bases concerned. It is of interest to mention that there is direct experimental evidence that the ionic product of liquid ammonia, and hence the basic dissociation constant of NH_3 , is small.¹⁹

¹⁹ Cf. K. Fredenhagen, *Z. anorg. Chem.*, **186**, 1 (1930).

Processes of class 2 include the transport of OH^- in water, as seen above, and of HSO_4^- in H_2SO_4 ; ²⁰ the latter can be represented by

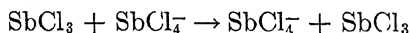


In agreement with expectation the HSO_4^- ion shows the greatest known abnormal conductance, since H_2SO_4 is a very strong acid. The small abnormalities observed for OR^- ions in the corresponding alcohols can be explained by the weakness of the $\text{R}\cdot\text{OH}$ acids. The anions F^- in HF , NH_2^- in NH_3 , and $\text{H}\cdot\text{CO}\cdot\text{O}^-$, $\text{CH}_3\cdot\text{CO}\cdot\text{O}^-$ and $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{O}^-$ in the respective acids have normal mobilities; the first two fit in with the general scheme since HF and NH_3 have low self-dissociation constants, but the behavior of the carboxylate ions is exceptional. The dissociation constants of the acids are sufficiently large for a high mobility to be expected, but it is possible that as a result of association of the molecules of acid, thus,

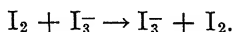


the speed of rotation is too small or the protons are too strongly bound to be transferred to an anion.

Fast reactions belonging to class 3 may include Cl^- in SbCl_3 ²¹ and I^- in I_2 , ²² although the experimental evidence, particularly in the latter case, is not conclusive. The mechanisms may be



and



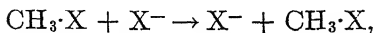
The mobilities of NO_2^- in $\text{CH}_3\cdot\text{NO}_2$ and of CNS^- in $\text{CH}_3\cdot\text{CNS}$ are both normal; if there were any abnormality, it would pre-

²⁰ L. P. Hammett and F. A. Lowenheim, *J. Am. Chem. Soc.*, **56**, 2620 (1934).

²¹ Z. Klemensiewicz, *Z. physik. Chem.*, **113**, 28 (1925); Z. Klemensiewicz and Z. Balówna, *Roczniki Chem.*, **10**, 481 (1930); **11**, 683 (1931).

²² G. N. Lewis and P. Wheeler, *Z. physik. Chem.*, **56**, 179 (1906); W. A. Piotnikow, J. A. Fialkow and W. P. Tschalij, *ibid.*, **A**, **172**, 304 (1935).

sumably be due to the process



where X represents NO_2 or CNS . Since the compounds $\text{CH}_3\cdot\text{NO}_2$ and $\text{CH}_3\cdot\text{CNS}$ do not ionize to any appreciable extent, the reactions must inevitably be slow and their contributions to the mobilities of the NO_2^- and CNS^- ions will be negligibly small.

ELECTRODE PHENOMENA

Static (Equilibrium) Electrode Potentials.—The discharge of an ion at a static electrode, *i.e.*, one at which there is no *net* flow of current, involves at least two stages, and hence two energy barriers. In the first place the solvated ion in the bulk

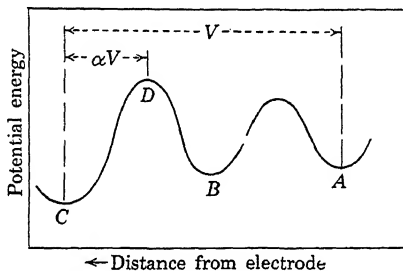


FIG. 135.—Potential-energy barriers at an electrode surface. (Kimball.)

of the solution must be transferred to the electrode surface, in which state it is probably unsolvated. Secondly, the adsorbed ion must combine with an electron, provided by the electrode, and thus be discharged. Other processes, such as migration of the resulting atom to a suitable position in the lattice, in the case of a metal, or the formation of molecules and their evolution as bubbles, in the case of a gas, generally follow; but these need not be considered for the moment. The potential-energy curve for the discharge of a positive ion, for example, may thus be represented, approximately, as in Fig. 135. The potential energy at A is that of an atom of the metal, B is that of the adsorbed ion and C represents that of the ion in solution. It is not known which of the two barriers is the higher, but this is immaterial for present purposes. The reverse process, *i.e.*, the conversion of an atom of metal into an ion in solution, follows the same two stages, *i.e.*, from A to B and B to C, in the opposite

direction; at equilibrium the forward and reverse reactions will occur at the same rate. When this condition is attained, the reversible potential V of the system will act between A and C , *i.e.*, across the two energy barriers; part of this potential will facilitate the discharge of the positive ions, and the remainder hinders the reconversion of atoms into ions.

In the absence of any external factor, such as the electrode potential, the specific rate k_1 of the discharge process, *i.e.*, the direct reaction, may be written, in terms of the theory of absolute reaction rates, as

$$k_1 = \frac{kT}{h} e^{-\Delta F_1^\ddagger/RT}, \quad (56)$$

and the specific rate k_2 of the reverse reaction is

$$k_2 = \frac{kT}{h} e^{-\Delta F_2^\ddagger/RT}, \quad (57)$$

where ΔF_1^\ddagger and ΔF_2^\ddagger are the corresponding free energies of activation. If α is the fraction of the potential V that is operative between the point C in Fig. 135 and the activated state, assumed to be at D , then the potential αV will facilitate the forward reaction. This means that there is a free-energy change of αVF per mole,* where F is the faraday, due to external factors, and hence the specific rate of the forward reaction becomes

$$k'_1 = k_1 e^{\alpha VF/RT}. \quad (58)$$

Similarly, the fraction $1 - \alpha$ of the reversible potential, *i.e.*, the portion acting between A and D , will retard the conversion of atoms into ions, and so the specific rate of the reverse reaction becomes

$$k'_2 = k_2 e^{-(1-\alpha)VF/RT}. \quad (59)$$

The actual rate of reaction is obtained by multiplying the specific rate by the activity of the reactant;† if the standard state chosen for the ionic species is the familiar one of a hypothetical ideal solution at unit concentration and that for the atoms is the pure solid, it follows that

$$\text{Rate of forward reaction} = a_+ k'_1 e^{\alpha VF/RT} \quad (60)$$

* For ions of valence of z , the corresponding free-energy term is $z\alpha VF$.

† The result should be divided by the activity coefficient of the activated complex; this cancels out when the rates at equilibrium are equated.

and

$$\text{Rate of reverse reaction} = k_2 e^{-(1-\alpha)VF/RT}, \quad (61)$$

where a_+ is the activity of the ions in the bulk of the given solution. The activity of the atoms on the electrode is, of course, unity in accordance with the chosen standard state. If V is the equilibrium reversible potential, which may now be represented by V_e , the two rates are equal, and hence

$$e^{-VF/RT} = a_+ \frac{k_1}{k_2} \quad (62)$$

$$= a_+ e^{-\Delta F^0/RT}, \quad (63)$$

where ΔF^0 , which is equivalent to $\Delta F_1^\ddagger - \Delta F_2^\ddagger$, is the standard free energy of the over-all direct process, *i.e.*, the transfer of ions from the solution to atoms on the electrode. It follows, therefore, that

$$V_e = \frac{\Delta F^0}{F} - \frac{RT}{F} \ln a_+, \quad (64)$$

the quantity $\Delta F^0/F$ being clearly equivalent to the standard potential V_0 of the electrode; thus,

$$V_e = V_0 - \frac{RT}{F} \ln a_+, \quad (65)$$

which is the familiar equation for the potential of a reversible electrode giving a univalent positive ion.*

Dynamic Electrode Potentials.²³—When there is a net flow of current at an electrode, the rate of one reaction exceeds that of the other; for example, at a cathode the rate of the forward, *i.e.*, discharge, process is greater than that of the reverse, *i.e.* ionization, process. The magnitude of the current flowing is determined by the difference in the two rates; thus, since each univalent ion carries a unit charge ε , the cathodic current I_e is given by Eq. (60) as

$$I_e = \varepsilon a k_1 e^{\alpha VF/RT}, \quad (66)$$

* It should be noted that the sign of the electrode potential V has been chosen in accordance with the convention proposed by G. N. Lewis and M. Randall ("Thermodynamics and the Free Energy of Substances," 1923) and adopted by many writers on physical chemistry. For the alternative convention, the term $e^{\alpha VF/RT}$ in Eq. (58) should be replaced by $e^{-\alpha VF/RT}$, and then (65) would become $V_e = V_0 + (RT/F) \ln a_+$.

²³ G. E. Kimball, *J. Chem. Phys.*, **8**, 199 (1940).

and the anodic current I_a is

$$I_a = \varepsilon k_2 e^{-(1-\alpha)VF/RT}, \quad (67)$$

and hence the net current, assumed to be cathodic, is

$$I = I_c - I_a = \varepsilon [ak_1 e^{\alpha VF/RT} - k_2 e^{-(1-\alpha)VF/RT}], \quad (68)$$

where a is written in place of a_+ for the activity of the positive ions in the immediate vicinity of the cathode. Since there is a flow of cathodic current, the concentration of positive ions in this region will be less than that in the bulk of the solution. The potential V will thus correspond to the activity a , which is less than that, represented by a_0 , existing in the body of the electrolyte.

The loss of ions from the vicinity of the electrode is made up partly by normal transport of ions by the current and partly by diffusion. If t_c is the transference number of the discharged cations, the rate at which ions are brought up by diffusion must be equivalent to $(1 - t_c)I$, *i.e.*, to tI where t is the effective transference number of all the other ions. If D is the diffusion coefficient of the ions (cations) being discharged and δ is the thickness of the so-called "diffusion layer," on one side of which the activity of the ions is a_0 whereas on the other it is a , the rate of diffusion is given by

$$\text{Rate of diffusion} = \frac{D}{\delta} (a_0 - a),$$

and hence the corresponding diffusion current I_d is

$$I_d = \frac{\varepsilon D}{\delta} (a_0 - a). \quad (69)$$

As seen above, this must be equal to tI ; and upon utilizing the value of I given by Eq. (68), it is seen that

$$t\varepsilon [ak_1 e^{\alpha VF/RT} - k_2 e^{-(1-\alpha)VF/RT}] = \frac{\varepsilon D}{\delta} (a_0 - a). \quad (70)$$

$$\therefore a = \frac{tk_2 e^{-(1-\alpha)VF/RT} + \frac{D}{\delta} a_0}{tk_1 e^{\alpha VF/RT} + \frac{D}{\delta}}. \quad (71)$$

If this value for a is inserted in Eq. (68), the result is

$$I = \frac{\varepsilon \frac{D}{\delta} [a_0 k_1 e^{\alpha VF/RT} - k_2 e^{-(1-\alpha)VF/RT}]}{t k_1 e^{\alpha VF/RT} + \frac{D}{\delta}} \quad (72)$$

$$\frac{\left(a_0 - \frac{k_2}{k_1} e^{-VF/RT} \right)}{t \frac{\delta}{D} + \frac{1}{k_1} e^{-\alpha VF/RT}} \quad (73)$$

According to Eqs. (62) and (63), k_1/k_2 is equal to $e^{-\Delta F^0/RT}$; and since, by Eqs. (64) and (65), ΔF^0 is equivalent to $V_0 F$, where V_0 is the standard potential of the electrode, it follows that

$$\frac{k_2}{k_1} = e^{\Delta F^0/RT} = e^{V_0 F/RT}, \quad (74)$$

and hence Eq. (73) may be written

$$I = \frac{\varepsilon [a_0 - e^{-(V-V_0)F/RT}]}{t \frac{\delta}{D} + \frac{1}{k_1} e^{-\alpha VF/RT}} \quad (75)$$

This equation should represent the variation of the electrode potential V with the current I , when the net flow of current is in the cathodic direction; as it is somewhat complicated, it may be simplified in two limiting cases. If k_1 is small, so that the discharge of the ions is the rate-determining stage, the term $t\delta/D$ may be neglected in the denominator of Eq. (75), and the latter then becomes

$$I = \varepsilon [a_0 k_1 e^{\alpha VF/RT} - k_2 e^{-(1-\alpha)VF/RT}]. \quad (76)$$

This is seen to be identical with Eq. (68), except that a_0 , the activity of the ions in the bulk of the solution, replaces a , the value in the immediate vicinity of the electrode; this condition can hold only for very small current strengths or, in the case of hydrogen-ion discharge, if the solution is well buffered.

The other limiting case, which is most frequently encountered, arises when the diffusion is the rate-determining stage of the electrode reaction. In these circumstances, k_1 is large and the term $k_1^{-1} e^{-\alpha VF/RT}$ in the denominator of Eq. (75) may be

neglected; hence,

$$I = \frac{\varepsilon D}{t\delta} [a_0 - e^{-(V-V_0)F/RT}]. \quad (77)$$

If both k_1 and k_2 are large, so that the cathode potential V is the reversible potential corresponding to the activity a of the ions in the immediate vicinity of the electrode, then it follows from Eq. (65) that $e^{-(V-V_0)F/RT}$ is equal to a ; hence, Eq. (77) may be written

$$I = \frac{\varepsilon D}{t\delta} (a_0 - a) \quad (78)$$

which is identical with (69).

The results derived above have been based on the assumption that the electrode is a cathode; if the anodic current exceeds the cathodic current, however, the net current will be given by the negative of Eq. (68); if the treatment already described is followed, the analogue of Eq. (75) is found to be

$$I = \frac{\varepsilon [e^{-(V-V_0)F/RT} - a_0]}{t \frac{\delta}{D} + \frac{1}{k_1} e^{-\alpha V F/RT}}, \quad (79)$$

and for diffusion-controlled anodic reactions,

$$I = \frac{\varepsilon D}{t\delta} [e^{-(V-V_0)F/RT} - a_0] \quad (80)$$

$$= \frac{\varepsilon D}{t\delta} (a - a_0). \quad (81)$$

In this case, since the electrode dissolves, the value of a , the activity in the vicinity of the anode, is in excess of that, a_0 , in the bulk of the electrolyte, so that $a - a_0$ is positive.

An interesting modification of Eq. (80) arises when a metal dissolves in an acid solution containing little or none of the ions of the metal; under these conditions, a_0 may be put equal to zero. Since most of the current is transported by the hydrogen ions, t is practically unity and so Eq. (80) becomes

$$I = \frac{\varepsilon D}{\delta} e^{-(V-V_0)F/RT}. \quad (82)$$

This gives the value of the anodic current resulting from the dissolution of the metal; an application of this relationship will be considered later.

THE THEORY OF OVERVOLTAGE

Introduction.—When an electrode, immersed in a solution of its own ions, or of the ions of a gas with which it is saturated, is at its reversible potential, the rate of deposition of ions on to the electrode is equal to the rate of re-ionization of the deposited substance; under these conditions, there is no net flow of current, and the resultant rate of deposition is zero. If material is to be deposited at an appreciable rate, or, in other words, in order that an appreciable current may flow from electrode to solution, or vice versa, it is necessary to impose an additional electrical potential on the system; the magnitude of this excess potential determines the net rate of deposition, *i.e.*, the current strength. The difference between the actual potential required to permit current to flow at a particular current density and the reversible value for the electrode in the given solution is called the “overvoltage” or “overpotential” at that current density.²⁴ In assessing the reversible potential, it is the general practice to suppose that the substances deposited are in their standard states; a gas, *e.g.*, hydrogen or oxygen, is supposed to be at 1 atm. pressure if this is the external pressure at which electrolysis occurs. The overvoltage obtained in this manner is, of course, important from the practical point of view; but for theoretical treatment it is preferable to define the overvoltage as the potential, under the experimental conditions, in excess of the reversible potential of the electrode *under the same conditions*. In this way, polarization phenomena resulting from changes in concentration of the electrolyte or from the fact that the solution may be supersaturated with gas, since this may be necessary before bubbles can form, are excluded from the true overvoltage. As the latter is probably related to the energy of activation of the slowest stage involved in the process of deposition of material on the electrode, it may be called the “activation overvoltage.”²⁵ The deposition of metals, except those of the iron group, generally requires only a small overvoltage, but appreciable values, rising sometimes to as much as 1 volt, accompany the liberation of hydrogen and oxygen.

²⁴ Cf. Glasstone, Ref. 2, Chap. XVII; *Ann. Rep. Chem. Soc.*, **34**, 107 (1937); F. P. Bowden and J. N. Agar, *ibid.*, **35**, 90 (1938); K. Wirtz, *Z. Elektrochem.*, **44**, 303 (1938).

²⁵ Bowden and Agar, Ref. 24; *Proc. Roy. Soc.*, **169**, A, 206 (1938).

The Rate-determining Step.—In the electrolysis of many aqueous solutions the over-all reaction is the conversion of water into hydrogen and oxygen, and the various stages involved at the cathode are as follows: (1) the transport of H_3O^+ ions to the electrode layer; (2) the transfer of ions or protons to the electrode; (3) discharge of the ions or protons by electrons; (4) the combination of the hydrogen atoms on the electrode surface to form molecular hydrogen; (5) the evolution of the hydrogen molecules in bubbles of gas. The slowest of these stages determines the overvoltage corresponding to a given current density. That stage 1 is not rate-determining is shown by the fact that the overvoltage depends on the nature of the metal used as cathode and is very small at an electrode of platinized platinum; further, the activation energy for the transport process is less than 3.5 kcal. (see page 566) which is much smaller than that usually associated with overvoltage (see Table LXXXVII, page 588). Although stage 5 probably plays some part, it is apparently of relatively minor importance in determining overvoltage; the evolution of chlorine gas bubbles, as a result of the electrolysis of chloride solutions, for example, requires only a small overvoltage. The suggestion that stage 4 is the slow process was originally made by J. Tafel,²⁶ but this view leads to expectations in disagreement with the facts. If the electrode surface is sparsely covered with atomic hydrogen, the rate of the reaction $2\text{H} = \text{H}_2$ is given by kn^2 , where k is a constant and n is the number of atoms of adsorbed hydrogen per square centimeter of electrode surface. If the rate of the reverse process, *i.e.*, the dissociation of hydrogen molecules into atoms, is negligible in comparison with that of the direct reaction, as it will be at appreciable current densities, the current flowing I is proportional to the rate of formation of molecular hydrogen; it is thus possible to write $I = kn^2$. The potential V of any atomic hydrogen electrode may be written in the form*

$$V = \frac{RT}{F} \ln n + \text{const.}, \quad (83)$$

²⁶ J. Tafel, *Z. physik. Chem.*, **54**, 641 (1905).

* Strictly speaking, the *activity*, and not the concentration, of atomic hydrogen should be used; under the conditions specified, however, *i.e.*, a sparsely covered surface, n is probably a measure of the activity.

where the constant depends on the hydrogen-ion concentration of the solution; the potential V_e of the reversible (equilibrium) electrode would then be

$$V_e = \frac{RT}{F} \ln n_e + \text{const.}, \quad (84)$$

n_e being the number of hydrogen atoms per square centimeter of surface at the reversible potential. The overvoltage ω , equal to $V - V_e$, is then given by

$$\omega = \frac{RT}{F} \ln \frac{n}{n_e}. \quad (85)$$

Combination of Eq. (85) with the result $I = kn^2$ then leads to the expression

$$I = kn_e^2 e^{2\omega F/RT} \quad (86)$$

or, more generally,

$$I = I_0 e^{2\omega F/RT} = I_0 e^{\alpha\omega F/RT}, \quad (87)$$

where I_0 is a constant and α is equal to 2. According to Eq. (87) the overvoltage at a given current density should be independent of the hydrogen-ion concentration, and this is, in general, true. Further, the plot of ω against $\ln I$ should be a straight line of slope $RT/2F$. But it has been found experimentally for a number of metals, that although the plot is linear, the slope is $2RT/F$; i.e., α in Eq. (87) is 0.5 instead of 2. In order to account for this discrepancy, it has been suggested that stage 3, viz., the neutralization of the hydrogen ion, is the slow process in the formation of gaseous hydrogen at an electrode and hence is the fundamental cause of overvoltage; it has been shown, on the basis of these views, that α might reasonably have the value 0.5 as found experimentally. Many workers in the field of overvoltage have, however, felt some difficulty in accepting the suggestion that the addition of an electron to a hydrogen ion or to a proton is a slow process requiring an activation energy of the order of 10 kcal. It appeared possible, therefore, that further insight into the mechanism of the hydrogen-electrode process might be obtained by applying the theory of absolute reaction rates.

Overvoltage and Absolute Reaction Rates.²⁷—According to Eq. (58), the specific rate k'_1 of the discharge of an ion under the influence of an electrode potential V is

$$k'_1 = k_1 e^{\alpha VF/RT}, \quad (88)$$

where k_1 is defined by

$$k_1 = \frac{kT}{h} e^{-\Delta F_1^\ddagger/RT}; \quad (88a)$$

but if this is applied to the problem of hydrogen-ion discharge, with V equal to the total potential operative between the solution and the cathode, it appears that the overvoltage should depend on the hydrogen-ion concentration at constant current density. There is much evidence, however, to show that, provided the hydrogen-ion concentration of the solution is not too low or the current density too large and extraneous ions are not present to any great extent, the overvoltage is independent of the pH of the electrolyte from which hydrogen-ion discharge occurs. It follows, therefore, in order to satisfy the experimental requirements, that in this instance the specific-rate equation should be written

$$k'_1 = k_1 e^{\omega F/RT}, \quad (89)$$

where ω is the overvoltage portion only of the total cathode potential.²⁸ The significance of this result is that, at least under the conditions where the overvoltage is independent of the hydrogen-ion concentration, the total electrode potential is operative across two double layers and that there are two potential-energy barriers.²⁹ The outer layer, which may be called the "solution double layer," is that at which the reversible hydrogen potential operates, whereas the overvoltage is effective over the inner, or "electrode double layer," close to the electrode. As long as there is no net flow of current, *i.e.*, if the amounts of current passing in both directions are the same,

²⁷ H. Eyring, S. Glasstone and K. J. Laidler, *J. Chem. Phys.*, **7**, 1053 (1939). A different application of the theory of absolute reaction rates, based on another mechanism, is given by G. Okamoto, J. Horiuti and K. Hirota, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **29**, 223 (1936).

²⁸ Cf. A. Frumkin, *Acta Physicochim. U.R.S.S.*, **12**, 481 (1940).

²⁹ G. E. Kimball, S. Glasstone and A. Glassner, *J. Chem. Phys.*, **9**, 91 (1941).

the potential across the electrode double layer is zero, and the fall of potential between the solution and the electrode is equal to that across the solution double layer, *i.e.*, the reversible potential. When there is a resultant flow of current, however, the electrical equilibrium across the electrode layer is disturbed and a difference of potential, equal to the overvoltage, is set up. If the slow stage in the discharge of hydrogen ions is the passage of protons across the electrode double layer, *i.e.*, if the potential-energy barrier closer to the electrode is the higher of the two (Fig. 136), there is no disturbance of equilibrium across the solution double layer, and the specific rate of the process will be

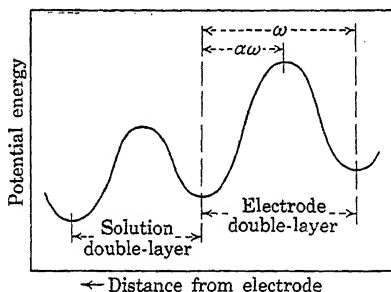


FIG. 136.—Representation of double layers at the electrode surface. (Kimball, Glasstone and Glassner.)

given by Eq. (89). It follows, therefore, that the specific rate of discharge of hydrogen ions, *i.e.*, the direct reaction, will be given by

$$k'_1 = k_1 e^{\alpha\omega F/RT}; \quad (90)$$

and, similarly, the specific rate of the reverse reaction is

$$k'_2 = k_2 e^{-(1-\alpha)\omega F/RT}, \quad (91)$$

since the fraction $(1 - \alpha)$ of the overvoltage operates *against* the formation of hydrogen ions from atoms. Without making any assumption as to the nature of the species from which the proton crossing the electrode double layer originates or that to which it proceeds, the respective concentrations or, more exactly, the activities of these substances may be represented by c_1 and c_2 units, respectively, the standard state being defined as 1 unit, *i.e.*, atom, molecule or ion, per square centimeter. The rates of forward (v_1) and reverse (v_2) reactions, in units per

square centimeter, may then be written

$$v_1 = c_1 k_1 e^{\alpha \omega F/RT} \quad (92)$$

and

$$v_2 = c_2 k_2 e^{-(1-\alpha)\omega F/RT}. \quad (93)$$

The current passing is determined by the difference between these rates; and if each reacting unit may be regarded as carrying the equivalent of a single charge, the current density I is given by

$$I = \varepsilon(v_1 - v_2) \quad (94)$$

$$= \varepsilon[c_1 k_1 e^{\alpha \omega F/RT} - c_2 k_2 e^{-(1-\alpha)\omega F/RT}], \quad (95)$$

where ε is the unit charge (*cf.* page 554). If ω is small, *i.e.*, for very low overvoltages, the exponentials may be expanded and all terms other than the linear one neglected; thus,

$$I = \varepsilon \left\{ c_1 k_1 \left(\frac{1 + \alpha \omega F}{RT} \right) - c_2 k_2 \left[1 - \frac{(1 - \alpha)\omega F}{RT} \right] \right\}. \quad (96)$$

It will be seen from Eqs. (92) and (93) that at the reversible potential, when ω is zero, $c_1 k_1$ is equal to $c_2 k_2$; and if this equality may be assumed to hold also for small values of ω , Eq. (96) becomes

$$I = \frac{\varepsilon c_1 k_1 \omega F}{RT}. \quad (97)$$

At low overvoltages, therefore, there should be a linear relationship between current and overvoltage; this has been found for the evolution of hydrogen and the deposition of metals.³⁰

For higher values of ω , the rate of the reverse reaction becomes negligibly small in comparison with that of the discharge process, so that it is possible to write

$$I = \varepsilon(c_1 k_1 e^{\alpha \omega F/RT}) = I_0 e^{\alpha \omega F/RT}, \quad (98)$$

where I_0 , whose significance will be seen shortly, is equal to $\varepsilon c_1 k_1$. This is identical with Eq. (87) and, as already seen,

³⁰ J. A. V. Butler, *Trans. Faraday Soc.*, **28**, 379 (1932); J. A. V. Butler and G. Armstrong, *J. Chem. Soc.*, 743 (1934); M. Volmer and T. Erdey-Grúz, *Z. physik. Chem.*, **A**, **159**, 165 (1931); M. Volmer and H. Wick, *ibid.*, **A**, **172**, 429 (1935).

applies at many cathodes, α having the value of 0.5. Since α is the fraction of the overvoltage effective between initial and activated states of the discharge process, it follows that the fall of potential between the initial and activated states must be, at least approximately, one-half that across the whole energy barrier;³¹ *i.e.*, the energy barrier at the electrode surface is almost symmetrical. This conclusion is of fundamental importance in deciding the nature of the essential electrode reaction.

Nature of Reacting Species.³²—The next matter to consider is the species involved in the electrode process; some information on this point may be obtained by calculating the value of c_1 , the concentration of this substance. According to Eq. (92) the magnitude of the current passing in the forward direction, *i.e.*, corresponding to the direct process, is

$$I \text{ (forward)} = \varepsilon(c_1 k_1 e^{\alpha \omega F/RT}); \quad (99)$$

and, at the reversible potential, when ω is zero, this becomes

$$I_0 = \varepsilon c_1 k_1 \quad (100)$$

$$= \varepsilon c_1 \frac{kT}{h} e^{-\Delta F_1^\ddagger/RT} \quad (101)$$

the definition of k_1 given on page 563 being used. Since ΔF^\ddagger may be replaced by $\Delta H^\ddagger - T \Delta S^\ddagger$, it follows that

$$I_0 = \varepsilon c_1 \frac{kT}{h} e^{\Delta S_1^\ddagger/R} e^{-\Delta H_1^\ddagger/RT} \quad (102)$$

$$= B e^{-\Delta H_1^\ddagger/RT}, \quad (103)$$

where B is equal to $\varepsilon c_1 (kT/h) e^{\Delta S_1^\ddagger/R}$; the quantities ΔS_1^\ddagger and ΔH_1^\ddagger are the entropy and heat of activation, respectively, of the direct electrode process. The value of I_0 may be determined by plotting $\ln I$, or $\log I$, against ω , obtained experimentally, for relatively high overvoltages, and then extrapolating to $\omega = 0$. The heat of activation ΔH_1^\ddagger can be derived from the temperature coefficient of overvoltage at constant overvoltage, provided that it is assumed that c_1 and ΔS_1^\ddagger are independent of temperature. From a knowledge of I_0 and ΔH_1^\ddagger , it is possible

³¹ T. Erdey-Grúz and H. Wick, *ibid.*, A, **162**, 53 (1932).

³² Eyring, Glasstone and Laidler, Ref. 27.

to calculate B , by means of Eq. (103), and the results obtained from the available experimental data³³ are recorded in Table LXXXVII. The measurements with cathodes of gallium and of Wood's alloy were made at 87°C., but all the other values of I_0 refer to 25°C.

TABLE LXXXVII.—DISCHARGE OF HYDROGEN IONS

Electrode	Electrolyte	$12 + \log I_0$	ΔH_1^\ddagger , kcal.	$\log B$
Mercury.....	0.2N H ₂ SO ₄	0.8	18.0	2.0
Mercury.....	0.2N NaOH	3.8	8.7	-1.8
Gallium.....	0.2N H ₂ SO ₄	5.2	15.2	2.5
Wood's alloy.....	0.2N H ₂ SO ₄	4.0	16.4	2.0
Bright platinum.....	0.2N H ₂ SO ₄	6.2	11.5	2.6
Bright platinum.....	0.2N H ₂ SO ₄	6.8	9.5	1.7
Bright platinum.....	0.2N NaOH	5.0	7.0	-1.9
Bright platinum.....	0.2N NaOH	6.3	6.0	-1.3
Palladium.....	0.2N H ₂ SO ₄	7.3	9.0	1.9
Palladium.....	0.2N NaOH	7.0	10.0	2.3

Except for the results with platinum in sodium hydroxide, which are stated to be very dependent on the condition of the surface, and with mercury in the same electrolyte, where the low value of α , *viz.*, 0.24, indicates the presence of complicating factors, *e.g.*, the discharge of sodium ions to form a dilute amalgam, the figures in the last column are virtually constant, and B , which involves c_1 and ΔS_1^\ddagger , is apparently independent of the nature of the electrode and electrolyte. This result suggests that the species whose concentration is represented by c_1 is *the same in all aqueous solutions and at all electrodes*, and the obvious conclusion to draw is that the substance is *water*. The provisional inference is, therefore, that the rate-determining step in the discharge of hydrogen ions involves a molecule of water. As a first approximation, it may be assumed that a water molecule occupies 10^{-15} sq. cm.; this is roughly the mean area of cross section of a single water molecule in pure water or of a metal atom of diameter 3 Å. The quantity c_1 would thus be about 10^{15} molecules per sq. cm.; and since kT/h at 25° is about 6×10^{12} and ε is 1.6×10^{-19} volt-coulombs, it

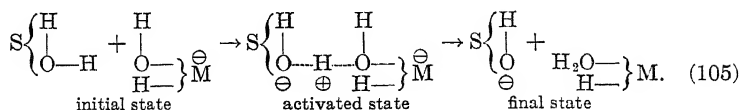
³³ Bowden and Agar, Ref. 24.

follows that

$$B = 9.6 \times 10^8 \times e^{\Delta S_1^\ddagger/R}. \quad (104)$$

Mechanism of Cathode Process.³⁴—To determine whether the assumption that a molecule of water is involved in the rate-determining stage is in harmony with the experimental value of B , it is necessary to assess ΔS_1^\ddagger , at least roughly; this can be done only if something is known of the nature of the initial and activated states. The next step, therefore, is to postulate a more detailed mechanism for the slow reaction at the cathode. It is suggested that the so-called "adsorption double layer," across which the overvoltage acts, consists of two layers of water molecules, one associated with the solution and the other held by the electrode. The slow stage in the discharge of a hydrogen ion is then believed to be the transfer of a proton from a molecule of water on the solution side to one attached to the electrode. The rate-determining step is then a kind of prototropic change; such processes are known to be associated with heats of activation of about 10 to 20 kcal. and hence are similar to those found for the cathodic liberation of hydrogen. Even when the proton has to move through a distance of the order of a molecular diameter, or less, as would be the case in the suggested cathode process, the heat of activation is of the same magnitude; this is proved by the stability at ordinary temperatures of the keto- and enol-forms of tautomeric compounds such as acetoacetic ester. It will be noted that according to the foregoing postulate the overvoltage acts across two layers of water molecules; and since it is probable that the activated state lies midway between them, the requirement that half the excess potential ω operates between the initial and activated states is satisfied.

The slow prototropic process, which is the essential cause of hydrogen overvoltage, may then be represented as follows:



The symbol S refers to the solution and M to the electrode surface, the \ominus sign on M being used to indicate an electron which

³⁴ Eyring, Glasstone and Laidler, Ref. 27.

is believed to be available at the cathode.* It is evident that the activated state consists virtually of H_3O^+ and OH^- ions, and it is apparent that the entropy of activation ΔS_1^\ddagger will be very close to that accompanying the transfer of a proton from one water molecule to another, *i.e.*, $\text{H}_2\text{O} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$; this process corresponds to the ionization of water in any aqueous solution. Taking $a_{\text{H}_3\text{O}^+} \times a_{\text{OH}^-}$ as 10^{-14} at 25° and $a_{\text{H}_2\text{O}}$ as 55 moles per liter, the equilibrium constant is found to be 3.3×10^{-18} ; since ΔH for the ionization of water is 13.6 kcal., it follows that $e^{\Delta S^\ddagger/R}$ is 3.3×10^{-8} . According to the foregoing arguments, therefore, $e^{\Delta S_1^\ddagger/R}$, required for the calculation of B by Eq. (104), should have the same value; hence, $\log B$ is approximately 1.5, in satisfactory agreement with the value found from overvoltage measurements (Table LXXXVII). The suggestion that the slow process at a cathode involves the transfer of a proton from one molecule of water to another is thus consistent with the experimental facts.

In the derivation of Eq. (104), it has been assumed that the concentration of water molecules is 10^{15} per square centimeter; strictly speaking, this applies to the layer attached to the solution, but the concentration on the electrode surface will probably be much the same. In other words the electrode is supposed to be completely covered with water molecules. If strictly true, this conclusion would be contrary to the observations made by various authors on the quantity of electricity required to change a hydrogen electrode to an oxygen electrode, and vice versa;³⁵ from these measurements, it appears that the former is covered with a layer of hydrogen and the latter with a layer of oxygen atoms. It must be remembered that neither the calculations on which this conclusion is based nor those in the present discussion are accurate within a factor of at least 2; it is not impossible that the electrode surface is covered to the

* The so-called "electrochemical mechanism," described by J. Horiuti and G. Okamoto [*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **28**, 231 (1936); K. Hirota and J. Horiuti, *Bull. Chem. Soc. Japan*, **13**, 228 (1938)], has some features in common with the foregoing scheme. Their theory, however, attributes overvoltage to the slow rate of neutralization of H_2^\ddagger .

³⁵ F. P. Bowden, *Proc. Roy. Soc.*, **125**, A, 446 (1929); J. A. V. Butler and G. Armstrong, *ibid.*, **137**, A, 604 (1932); G. Armstrong, F. R. Himsworth and J. A. V. Butler, *ibid.*, **143**, A, 89 (1933); A. Frumkin and A. Slygin, *Acta Physicochim. U.R.S.S.*, **5**, 89 (1936); B. Ershler, *ibid.*, **7**, 327 (1937).

extent of one-half, or of that order, by water molecules and the remainder by hydrogen or oxygen atoms.

Influence of Electrode Material.—If the value of I_0 given by Eq. (102) is introduced into (98), it is seen that

$$I = \varepsilon C_1 \frac{kT}{h} e^{\Delta S_1^\ddagger/R} e^{-\Delta H_1^\ddagger/RT} e^{\alpha n F/RT}. \quad (106)$$

In the absence of strongly adsorbed substances, it appears that the different overvoltages of various metals must be attributed to differences in ΔH_1^\ddagger , the heat of activation of the rate-determining process; the higher the value of ΔH_1^\ddagger , the greater the overvoltage. If the metal is one that adsorbs hydrogen readily,

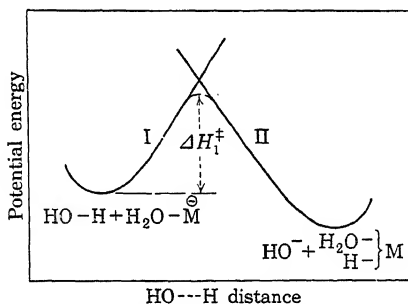


FIG. 137.—Potential-energy curves for the transfer of a proton at a cathode. (Eyring, Glasstone and Laidler.)

i.e., it forms strong M—H bonds, then the oxygen atom of a water molecule held on such a surface will have increased affinity for the formation of a bond with hydrogen; the attachment of a proton to the oxygen atom will, therefore, be facilitated, and the heat of activation of the prototropic change responsible for overvoltage will be relatively low. This conclusion will be apparent from a consideration of the potential-energy curves for the initial and final states of the rate-determining process (Fig. 137).³⁶ If the metal attracts the water molecule by forming strong M—H bonds, thus increasing the attraction of the proton, curve I will be less steep and ΔH_1^\ddagger will be diminished. Further, if the electrode material adsorbs atomic hydrogen

³⁶ Cf. J. Horiuti and M. Polanyi, *Acta Physicochim. U.R.S.S.*, **2**, 505 (1935); J. Horiuti and G. Okamoto, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **28**, 231 (1936); J. A. V. Butler, *Proc. Roy. Soc.*, **157**, A, 423 (1936); *Z. Elektrochem.*, **44**, 55 (1938).

readily, the position of curve II will be lowered, and this will also have the effect of decreasing ΔH_1^\ddagger and hence the overvoltage. Metals, such as platinum, palladium, copper, nickel, iron and silver, which adsorb hydrogen strongly, should thus have low overvoltages, in agreement with experiment; these substances are, as may be expected, good catalysts for the $2H = H_2$ reaction, but this is not to be taken as evidence for the view that atomic hydrogen is responsible for overvoltage as was at one time suggested. The elements mercury, lead, zinc, tin and cadmium form only feeble M—H bonds, and hence these metals have high overvoltages. They should be poor catalysts for the recombination of atomic hydrogen, and this has been verified for lead.

The constancy of the quantity B in Table LXXXVII and the prototropic theory of overvoltage imply that the concentration of water molecules per *apparent* square centimeter of electrode surface is approximately constant; this can be true, however, only if the surface is relatively smooth and the apparent and real areas are not very different. If the electrode surface is roughened, however, the quantity c_1 will be increased and as a consequence the overvoltage at an *apparent* constant current density will decrease. It is well known that roughening an electrode surface decreases the overvoltage, but it is possible that other factors besides mere increase of surface are responsible. The number of active adsorption centers probably increases more rapidly than does the actual surface area. Further, especially active centers may be developed; this is probably true for platinized platinum electrodes.

Alternative Electrode Processes.—The model proposed here does not, of course, exclude the possibility that in certain circumstances other steps in the discharge process may become rate-determining; for example, on some electrodes the combination of atomic hydrogen to form molecules may be the slowest process. Since α is very close to 0.5 at electrodes of mercury, gallium, silver, nickel, etc., it is unlikely that the recombination reaction is the cause of overvoltage in these cases; but when α is large, for example, at platinum, copper and palladium, under certain conditions, where values of 0.8 and more have been observed,³⁷

³⁷ C. A. Knorr and E. Schwartz, *ibid.*, **40**, 38 (1934); *Z. physik. Chem.*, **A**, **176**, 161 (1936); M. Volmer and H. Wick, *ibid.*, **A**, **172**, 429 (1935); K. Wirtz, *ibid.*, **B**, **36**, 435 (1937).

it is possible that this process is of importance in determining the current strength at a given overvoltage. When the electrode forms very strong M—H bonds, the heat of activation of the prototropic process may become so low that the reaction $2\text{H} = \text{H}_2$ becomes the rate-determining step. According to Tafel's calculations (page 582), α should then become equal to 2, and values of α between 2 and 0.5 are presumably due to the fact that the combination of atoms and the prototropic change have velocities of the same order; hence, both are effective in determining the rate of discharge of hydrogen ions. As the overvoltage is raised, the rate of atom combination increases as the exponential of twice the overvoltage and that of the prototropic reaction as the exponential of half the overvoltage; the former process will thus become very rapid as compared with the latter. It is evident, therefore, that the combination of atomic hydrogen can only be rate-determining, and hence the ultimate cause of overvoltage, when the latter is small.³⁸

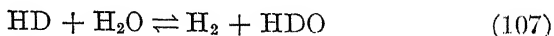
It may be remarked that according to the prototropic mechanism of overvoltage α is only 0.5 if the energy barrier is approximately symmetrical and the potential fall is uniform. If for any reason there is distortion, then α may fall to zero if the activated state is pushed out toward the solution or increase to unity if it approaches the electrode more closely.

Separation of Hydrogen and Deuterium.—The electrolytic separation of hydrogen and deuterium is attributed to the difference in overvoltage for the deposition of the two isotopic forms, and the expected larger value for deuterium has been confirmed experimentally. It is necessary to demonstrate, therefore, that the higher overvoltage for deuterium is consistent with the theory developed above. The free energy of ionization of deuterium oxide, *i.e.*, $\text{D}_2\text{O} + \text{D}_2\text{O} = \text{D}_3\text{O}^+ + \text{OD}^-$, calculated from the known ionic product, is about 1,000 cal. greater than for ordinary water; and hence it may be supposed that the free activation energies for the transfer of a deuteron and a proton at a cathode differ by a similar amount. Upon utilizing the method described on page 587 and making the same assumptions, it is found that ΔS_1^\ddagger is almost identical for proton and deuteron transfer; hence it follows that the heat of activation for the deuterotropic change must be approximately 1,000 cal.

³⁸ L. P. Hammett, *Trans. Faraday Soc.*, **29**, 770 (1933).

greater than for the cathodic prototropic change. On the assumption that the difference is actually 1,200 cal., it can be readily calculated that the specific rate of the discharge process involving hydrogen is 7.4 times as great as that for deuterium; this is of the correct order to account for the observed separation coefficients. From the limited data available, it appears that ΔH_1^\ddagger for hydrogen evolution from 0.2 *N* sulfuric acid at a mercury cathode is 18.0 cal., whereas for deuterium discharge it is 20.9 kcal. If ΔS_1^\ddagger for the cathodic process is the same for the transfer of a proton and a deuteron, as the approximate calculations suggest, then the difference in the ΔH^\ddagger values is larger than expected. From the value of ΔH_1^\ddagger for deuterium, $\log B$ is found to be 3.24, which is higher than the results in Table LXXXVII; if the heat of activation for deuterium evolution is assumed to be 19.2 kcal., however, *i.e.*, 1,200 cal. larger than for hydrogen, $\log B$ is calculated as almost exactly 2.0. A difference of 1,200 cal., rather than 2,900 cal., in the heats of activation would thus be consistent with the mechanism of hydrogen discharge proposed in this chapter, and the subject merits further experimental investigation. If the zero-point energies of the activated states do not differ greatly, the difference in the heats of activation for deuterotropic and prototropic reactions should be equal to the difference in the zero-point energies of the D—O and H—O bonds, *i.e.*, about 1,400 cal. This is also in harmony with the arguments given above.

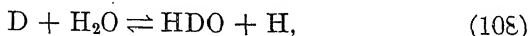
It is of interest that the hydrogen-deuterium separation factors obtained with different metals fall roughly into the same two groups as do overvoltages themselves; at low-overvoltage metals, *e.g.*, platinum, nickel and silver, the separation coefficient is about 6, whereas at high-overvoltage electrodes, *e.g.*, lead (in acid solution), mercury and tin, the value is in the vicinity of 3.³⁹ The latter figure is very close to that expected if the equilibrium



were established at the cathode, and this is presumably what happens on high-overvoltage metals. It has been seen that

³⁹ B. Topley and H. Eyring, *J. Chem. Phys.*, **2**, 217 (1934); Horiuti and Okamoto, *Ref. 36*; H. F. Walton and J. H. Wolfenden, *Trans. Faraday Soc.*, **34**, 436 (1938).

elements of this type form only weak M—H bonds, so that the hydrogen and deuterium atoms on the surface, liberated by electrolysis, have a high energy content and hence are reactive. It is probable, therefore, that the surface reaction



which will lead to the establishment of equilibrium conditions, takes place rapidly on a high-overvoltage electrode. In order that complete equilibrium may be established, it is necessary that the HDO molecule, which is presumably attached to the electrode as OH and D (or OD and H), should be able to leave the surface readily and exchange with H₂O molecules; this will occur if the bonds holding the OH (or OD) and D (or H) to the surface are weak in comparison with the O—D (or O—H) bond. It is just at high-overvoltage electrodes, where the strength of the M—H bond is small, that this condition is satisfied. At low-overvoltage cathodes the activity of the hydrogen will be small and there will be little tendency for the equilibrium (107) to be attained.

Not only will increase of temperature increase the specific rate of reaction (108), but it will also speed up the recombination of hydrogen atoms on the surface and hence decrease their concentration. If the heats of activation of the two processes are such that the first reaction is favored more than the second when the temperature is raised, then there will be a closer approach to equilibrium and the separation factor will decrease; this is the case at platinum, nickel and silver cathodes. On the other hand, if increase of temperature favors the atom-recombination process, so that there is a marked decrease in the concentration of atomic deuterium on the surface, the equilibrium state will be less readily attained and the separation factor may rise; a result of this type has been observed with a tin cathode.⁴⁰

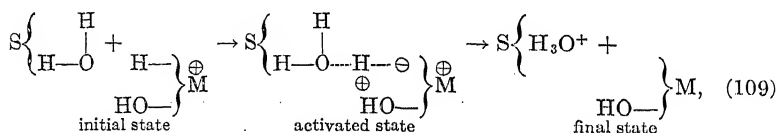
At a platinized platinum cathode the separation factor is about 3, in spite of the low overvoltage; at this electrode, however, departure from equilibrium can never be very appreciable, for on a platinized surface water reacts relatively rapidly even with molecular deuterium, or HD. The separation factor is thus

⁴⁰ Walton and Wolfenden, Ref. 39.

never likely to differ to any great extent from the theoretical value based on the assumption that equilibrium is attained.

Although the hydrogen-deuterium separation coefficient is generally independent of the hydrogen-ion concentration of the electrolyte, at a lead electrode it is as high as 6 in an alkaline solution as compared with 3 in acid solution; it may be significant that the overvoltage of lead is definitely less in media of high pH than in acid solution, and cathodic reduction is generally more efficient in an acid electrolyte. The presence of excess of hydroxyl ions, however, also produces other changes in the conditions at an electrode surface.

Oxygen Overvoltage.⁴¹—Interaction between the evolved oxygen and the electrode material leads to complications in the study of anodic phenomena, but in spite of the difficulties it has become evident that there is a fundamental similarity between the processes occurring at anode and cathode. The kinetics of the deposition of oxygen bears a marked resemblance to that for hydrogen evolution, and both in acid and dilute alkaline solutions the variation of oxygen overvoltage with current density at a platinum anode is given by Eq. (98) with α having a value of approximately 0.5, as for hydrogen-ion discharge.⁴² The results are in agreement with the suggestion that the rate-determining process for oxygen evolution is a prototropic change, similar to that postulated for hydrogen evolution but in the opposite direction. A proton from a water molecule attached to the surface is transferred to one in the layer associated with the electrolyte; thus,



the sign \oplus on M representing the deficit of an electron. The hydroxyl radicals formed on the surface react in pairs with the ultimate formation of molecular oxygen, the intermediate stage or stages being relatively rapid. The connection between oxygen and hydrogen overvoltage is at once evident, and the

⁴¹ Eyring, Glasstone and Laidler, Ref. 27.

⁴² F. P. Bowden, *Proc. Roy. Soc.*, **126**, A, 107 (1929); F. P. Bowden and H. W. Keenan, see Bowden and Agar, Ref. 24.

fact that α in Eq. (98) is about 0.5 in both cases is readily understood. If this mechanism for the slow process in oxygen evolution is correct, the value of $\log B$ should not be of a very different order from those in Table LXXXVII. The only experimental data that permit the calculation to be made are those for a platinum anode in dilute sulfuric acid solution: $12 + \log I_0$ is 1.57, and ΔH_1^\ddagger is 18.7 kcal. at 14°C., and so $\log B$ is 3.83. This value is somewhat larger than for hydrogen evolution; but, in view of the uncertainties associated with the nature of the anode, the agreement is reasonably good.

If there were no formation of surface oxides, it would be expected that metals forming strong M—H bonds should have high overvoltages, since the attraction would tend to hinder the removal of a proton from the surface. It is true that smooth platinum, palladium and gold, which have the lowest hydrogen overvoltages, have the highest overvoltages for oxygen evolution, but the parallelism does not always hold. Nickel and cobalt, for example, have low overvoltages at both the anode and the cathode; the oxidation of the surface is undoubtedly a complicating factor.

Overvoltage and Dissolution of Metals.⁴³—When a metal dissolves in an acid solution containing practically none of the cations of the metal, the magnitude of the anodic current is given by Eq. (82) for univalent ions, provided that diffusion is the rate-determining process. In general, for z -valent ions, the value of the anodic current is

$$I_a = \frac{z\epsilon D}{\delta} e^{-z(V-V_0)F/RT}, \quad (110)$$

where V is the potential of the dissolving metal in the given solution and V_0 is its standard potential. Since the electrode is not coupled with another, there is no actual flow of current; and so the anodic current I_a must be exactly balanced by the cathodic current I_c , resulting from the discharge of hydrogen ions. If the current due to the passage of hydrogen gas into solution as ions is neglected (*cf.* page 582), I_c is given by Eq. (98) which may be written in the form

$$I_c = 8k_1 a_{\text{H}_2\text{O}} e^{\alpha\omega F/RT}, \quad (111)$$

⁴³ G. E. Kimball and A. Glassner, unpublished.

where c_1 has been replaced by $a_{\text{H}_2\text{O}}$ since, according to the theory of hydrogen overvoltage developed above, it is equivalent to the concentration (or activity) of water at the surface of the electrode. If the facts are utilized that ω is equal to $V - V_e$, where V is the actual potential and V_e the reversible (equilibrium) potential of the hydrogen electrode in the given solution and that V_e is equal to $-(RT/F) \ln a_{\text{H}_3\text{O}^+}$, on the assumption that the standard potential of hydrogen is zero, it follows from Eq. (111) that

$$I_c = sk_1 a_{\text{H}_2\text{O}} a_{\text{H}_3\text{O}^+}^\alpha e^{\alpha VF/RT}. \quad (112)$$

When the dissolving metal has reached a steady state, the values of I_c and I_a as given by Eqs. (110) and (112) must be equal, the potential V being the same in both cases; hence,

$$\frac{zD}{\alpha} e^{-z(V-V_0)/RT} = k_1 a_{\text{H}_2\text{O}} a_{\text{H}_3\text{O}^+}^\alpha e^{\alpha VF/RT} \quad (113)$$

Upon solving this equation for V , it is found that

$$V = \frac{zV_0}{z + \alpha} - \frac{RT}{(z + \alpha)F} (Q + \ln a_{\text{H}_2\text{O}} + \alpha \ln a_{\text{H}_3\text{O}^+}), \quad (114)$$

where Q is a constant for the given metal, equal to $\delta k_1/zD$. Since $a_{\text{H}_2\text{O}}$ may be taken as constant, it follows that

$$V = C - \frac{\alpha RT}{(z + \alpha)F} \ln a_{\text{H}_3\text{O}^+}, \quad (115)$$

where C is a constant. The plot of the electrode potential V against the pH of the solution, *i.e.*, $-\ln a_{\text{H}_3\text{O}^+}$, should thus be a straight line of slope $\alpha RT/(z + \alpha)F$. It has been seen that α is generally 0.5; hence, for a bivalent metal *i.e.*, z is 2, the slope should be about 0.012 at ordinary temperatures; this has been confirmed in experiments on the dissolution of cadmium in acid solutions. For solutions of relatively low acidity, the term $\alpha \ln a_{\text{H}_3\text{O}^+}$ in Eq. (114) may be neglected in comparison with $Q + \ln a_{\text{H}_2\text{O}}$, and hence it appears that under these conditions the potential of the dissolving metal should become independent of the pH of the attacking solution; this expectation has been realized experimentally for cadmium over a range of relatively high pH values.

PHOTOVOLTAIC POTENTIALS⁴⁴

Influence of Light Intensity.—When an electrode that exhibits a photovoltaic effect is illuminated, the electrons liberated by the action of the light discharge a number of positive ions proportional in amount to the intensity of the radiation; an additional anodic current, equal to sk_3J , where J is the light intensity, must then be included in Eq. (68). Following through the treatment given on pages 577 *ff.*, the corresponding form of Eq. (77), *i.e.*, when diffusion is rate-determining, is

$$I = k_4 - k_5 e^{-(V-V_0)F/RT} - k_6J, \quad (116)$$

where k_4 , k_5 and k_6 are constants for a given electrode and electrolyte. If there is no actual flow of current, so that I is zero, then

$$k_6J = k_4 - k_5 e^{-(V-V_0)F/RT}. \quad (117)$$

The electrode potential V will, however, differ from the equilibrium potential V_e of the system, the difference $V_e - V$ being equal to ϕ , the magnitude of the photovoltaic effect. Since $e^{-(V_e-V_0)/RT}$ is a constant determined by the concentration of the solution, it follows from Eq. (117) that

$$k_6J = k_4 - k_7 e^{\phi F/RT}; \quad (118)$$

$$\therefore \phi = A + B \ln J, \quad (119)$$

where A and B are constants. The photovoltaic effect should thus be a logarithmic function of the light intensity; this result is in agreement with experiment for electrodes coated with oxides or sulfides of gold or copper. When the photovoltaic effect is small, *e.g.*, at low light intensities or for pure metals, $e^{\phi F/RT}$ may be replaced by $1 + \phi/RT$, when it is found that

$$\phi = A' + B'J, \quad (120)$$

so that the photovoltaic potential is a linear function of the light intensity; this is also in harmony with observation.

⁴⁴ E. Adler, *J. Chem. Phys.*, **8**, 500 (1940).

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